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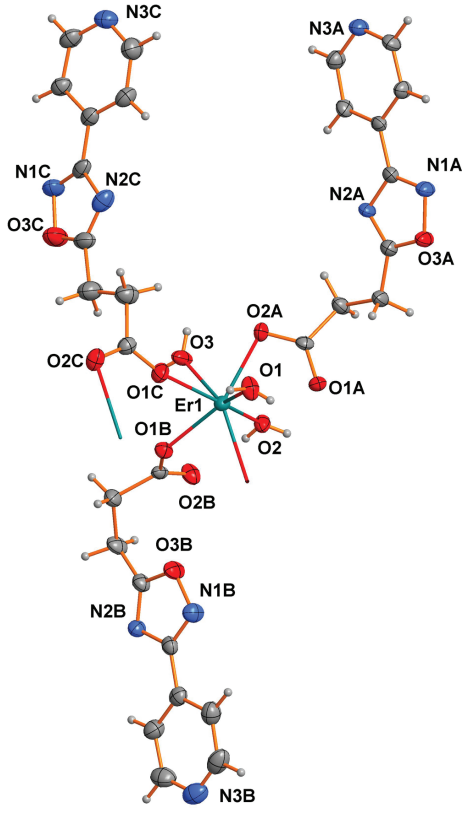
The crystal structure of hexaaqua-bis(μ$_2$-3-(3-(pyridin-4-yl)-1,2,4-oxadiazol-5-yl)propanoato-κ^2*O*:*O*′)-tetrakis(3-(3-(pyridin-4-yl)-1,2,4-oxadiazol-5-yl)propanoato-κ*O*)dierbium(III) octahydrate, $C_{60}H_{76}N_{18}O_{32}Er_2$



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Abstract

$C_{60}H_{76}N_{18}O_{32}Er_2$, monoclinic, $P2_1/n$ (no. 14), $a = 10.5441(4)$ Å, $b = 31.1092(9)$ Å, $c = 12.0993(4)$ Å, $\beta = 114.398(4)°$, $V = 3614.4(2)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0431$, $wR_{ref}(F^2) = 0.0805$, $T = 296(2)$ K.

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The asymmetric unit (without solvent water molecules) of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Needle, pink
Size:	0.42 × 0.23 × 0.18 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	2.41 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
θ_{max}, completeness:	26°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16106, 7077, 0.033
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6216
$N(param)_{refined}$:	505
Programs:	Bruker programs [1], SHELX [2]

Source of material

3-(3-Pyridin-4-yl-[1,2,4]oxadiazol-5-yl)-propionic acid (*HL*) is easily available by a literature known synthesis [3]. A solution of ammonia (0.5 M) was added dropwise to a methanol (15 mL) solution of HL (3 mmol), resulting in a transparent solution. A methanol (15 mL) solution of zinc acetate dihydrate (1.5 mmol) was added into the solution and allowed to stir for 3 h, resulting in a suspension. A methanol (15 mL) solution of erbium nitrate hexahydrate (1 mmol) was added into the suspension and allowed to stir for 8 h. The suspension was filtered and diethyl ether was allowed to diffuse slowly into the solution of the filtrate. Crystals were obtained in about 4 weeks.

Experimental

H atoms bound to C atoms were placed in calculated positions and treated as riding on their parent atoms, with C—H = 0.93 or 0.97 Å and U_{iso} (H) = 1.2 or 1.5 U_{eq}(C). H atoms of water molecule were initially found in the difference Fourier map and were refined with restraint as O—H = 0.85 Å. Three

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

Atom	x	y	z	U_{iso}*/U_{eq}
C1A	0.9145(5)	0.56796(14)	0.5526(4)	0.0247(10)
C1B	0.4908(5)	0.46657(13)	0.1819(4)	0.0256(10)
C1C	0.3815(5)	0.56878(15)	0.4769(4)	0.0313(11)
C2A	1.0281(5)	0.60085(15)	0.5793(4)	0.0340(11)
H2A1	0.9857	0.6291	0.5589	0.041*
H2A2	1.0755	0.5953	0.5270	0.041*
C2B	0.3527(5)	0.44697(16)	0.0981(5)	0.0370(12)
H2B1	0.2994	0.4685	0.0392	0.044*
H2B2	0.3010	0.4396	0.1457	0.044*
C2C	0.3937(6)	0.61668(17)	0.4493(5)	0.0480(14)
H2C1	0.3720	0.6346	0.5048	0.058*
H2C2	0.4881	0.6230	0.4599	0.058*
C3A	1.1352(5)	0.60152(15)	0.7098(5)	0.0396(13)
H3A1	1.1020	0.5838	0.7585	0.048*
H3A2	1.2211	0.5889	0.7138	0.048*
C3B	0.3645(5)	0.40694(16)	0.0302(4)	0.0384(12)
H3B1	0.2727	0.3996	−0.0305	0.046*
H3B2	0.4230	0.4135	−0.0119	0.046*
C3C	0.2962(7)	0.62563(18)	0.3241(6)	0.0558(16)
H3C1	0.2035	0.6170	0.3134	0.067*
H3C2	0.3219	0.6084	0.2697	0.067*
C4A	1.1646(5)	0.64523(15)	0.7625(4)	0.0307(11)
C4B	0.4225(5)	0.36937(16)	0.1084(4)	0.0316(11)
C4C	0.2932(6)	0.67274(16)	0.2895(6)	0.0423(13)
C5A	1.1782(4)	0.70986(14)	0.8090(4)	0.0271(10)
C5B	0.4891(5)	0.30881(15)	0.1857(4)	0.0303(11)
C5C	0.2995(5)	0.73899(16)	0.2729(5)	0.0343(12)
C6A	1.1528(4)	0.75669(14)	0.8009(4)	0.0259(10)
C6B	0.5043(5)	0.26220(16)	0.1961(5)	0.0322(11)
C6C	0.3305(5)	0.78504(15)	0.2995(5)	0.0318(11)
C7A	1.2204(5)	0.78305(15)	0.9011(4)	0.0325(11)
H7A	1.2802	0.7715	0.9753	0.039*
C7B	0.4358(5)	0.23645(16)	0.0962(5)	0.0401(12)
H7B	0.3778	0.2486	0.0222	0.048*
C7C	0.4314(5)	0.79821(17)	0.4085(5)	0.0414(13)
H7C	0.4809	0.7783	0.4682	0.050*
C8A	1.1965(5)	0.82646(15)	0.8875(5)	0.0349(11)
H8A	1.2424	0.8440	0.9545	0.042*
C8B	0.4543(6)	0.19258(18)	0.1071(6)	0.0503(15)
H8B	0.4065	0.1756	0.0392	0.060*
C8C	0.4575(6)	0.84132(19)	0.4271(5)	0.0500(14)
H8C	0.5260	0.8499	0.5015	0.060*
C9A	1.0459(5)	0.81963(16)	0.6906(5)	0.0355(11)
H9A	0.9848	0.8321	0.6183	0.043*
C9B	0.6023(6)	0.1981(2)	0.3045(6)	0.0517(15)
H9B	0.6612	0.1852	0.3768	0.062*
C9C	0.2942(6)	0.85876(16)	0.2424(5)	0.0426(13)
H9C	0.2465	0.8795	0.1847	0.051*
C10A	1.0631(5)	0.77542(15)	0.6939(4)	0.0315(11)
H10A	1.0151	0.7588	0.6254	0.038*
C10B	0.5893(5)	0.24221(18)	0.3034(5)	0.0446(13)
H10B	0.6366	0.2582	0.3734	0.054*
C10C	0.2593(5)	0.81624(15)	0.2148(5)	0.0361(12)
H10C	0.1890	0.8086	0.1405	0.043*
Er1	0.66356(2)	0.517714(6)	0.448817(19)	0.02577(7)
N1A	1.2701(4)	0.69256(12)	0.9072(4)	0.0354(10)
N1B	0.5563(4)	0.33476(14)	0.2750(4)	0.0393(10)
N1C	0.2221(5)	0.72612(14)	0.1648(5)	0.0483(12)
N2A	1.1107(4)	0.68175(12)	0.7160(4)	0.0302(9)
N2B	0.4041(4)	0.32905(12)	0.0798(4)	0.0306(9)
N2C	0.3491(5)	0.70596(15)	0.3572(4)	0.0456(11)
N3A	1.1114(4)	0.84504(13)	0.7842(4)	0.0360(10)
N3B	0.5369(5)	0.17316(15)	0.2098(5)	0.0520(13)
N3C	0.3929(5)	0.87161(14)	0.3476(4)	0.0469(12)
O1	0.7283(3)	0.52209(11)	0.6601(3)	0.0390(8)
H11	0.7828	0.5096	0.6981	0.058*
H12	0.6639	0.5194	0.6889	0.058*
O1A	0.9427(3)	0.52962(9)	0.5816(3)	0.0291(7)
O1B	0.4964(3)	0.48242(10)	0.2801(3)	0.0281(7)
O1C	0.4773(3)	0.54411(11)	0.4802(3)	0.0373(8)
O2	0.7945(3)	0.50411(10)	0.3364(3)	0.0312(7)
H21	0.7483	0.4936	0.2748	0.047*
H22	0.8651	0.4944	0.3584	0.047*
O2A	0.7902(3)	0.58059(10)	0.4956(3)	0.0353(8)
O2B	0.5888(3)	0.46649(11)	0.1499(3)	0.0360(8)
O2C	0.2806(3)	0.55549(11)	0.4960(3)	0.0390(8)
O3	0.5682(3)	0.56633(10)	0.2831(3)	0.0399(9)
H31	0.5882	0.5904	0.2829	0.060*
H32	0.5135	0.5593	0.2300	0.060*
O3A	1.2610(3)	0.64836(10)	0.8768(3)	0.0349(8)
O3B	0.5117(4)	0.37571(11)	0.2249(3)	0.0394(8)
O3C	0.2178(4)	0.68120(12)	0.1752(4)	0.0565(11)
O4	0.3586(4)	0.55722(13)	0.0529(3)	0.0533(10)
H41	0.3783	0.5509	−0.0038	0.080*
H42	0.2745	0.5607	0.0312	0.080*
O5	0.9491(4)	0.47513(13)	0.8297(4)	0.0605(11)
H51	0.9355	0.4663	0.8879	0.091*
H52	0.9857	0.4597	0.7964	0.091*
O6	0.5554(4)	0.94695(13)	0.4518(4)	0.0575(11)
H61	0.5138	0.9243	0.4255	0.086*
H62	0.5280	0.9667	0.4028	0.086*
O7	0.5962(4)	0.08174(13)	0.2504(4)	0.0600(11)
H71	0.5845	0.1079	0.2447	0.090*
H72	0.6323	0.0651	0.2194	0.090*

residual peaks in the vicinity of Er atom are thought as ghost peaks of Er atom.

Discussion

Lanthanide-based carboxylate complexes have been found to exhibit anticancer properties, unusual coordination characteristics, exceptional optical, magnetic properties [4–8] and so on. As an ongoing part of our investigations, we report the preparation and crystal structure of the title compound.

In the dimeric structure unit of title complex, there are four water solvent molecules, three ligands adopt monodentate mode, and a chelating bidentate mode, respectively. Two neighboring Er^{III} ions form a dinuclear complex with the Er1-Er1 distance of 4.2632(4) Å by way of two oxygen atoms of carboxylates act as the bridge (chelating bidentate mode),

and the Er^{III} ions are seven-coordinated by six oxygen atoms from three water molecules, and four O-atoms from four different carboxylates (*cf*. the figure). The Er-O bond lengths, depending on the nature of the O-atoms, vary from 2.303(3) to 2.378(3) Å. There is a second coordination sphere with Er-O distances of ~2.75 Å. The dimeric structural unit further connected by intermolecular hydrogen bonds. Such a structure is isostructural with its rare earth analogues [9, 10].

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References

1. Bruker. APEX2, SAINT and SADABS. Brucker AXS Inc., Madison, WI, USA (2009).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Zhang, F.; Liu, F.; Chen, Q. F.; Dong, M. D.: 3-[3-(Pyridin-3-yl)-1, 2, 4-oxadiazol-5-yl]propanoic acid. Acta Crystallogr. **E67** (2011) o193.
4. Kido, J.; Okamoto, Y.: Organo lanthanide metalcomplexes for electrolu-minescent materials. Chem. Rev. **102** (2002) 2357–2368.
5. Marques, N.; Sella, A.; Takats, J.: Chemistry of the lanthanides using pyrazolylborate ligands. Chem. Rev. **102** (2002) 2137–2159.
6. Zaleski, C. M.; Depperman, E. C.; Kampf, J. W.; Kirk, M. L.; Pecoraro, V. L.: Synthesis, structure, and magnetic properties of a large lanthanide-transition metal single-molecule magnet. Angew. Chem. Int. Ed. **43** (2004) 3912–3914.
7. Muro, I. G.; Mautner, F. A.; Insausti, M.; Lezama, L.; Arriortua, M. I.; Rojo, T.: Study of the two-dimensional $[MM'(C_3H_2O_4)_2(H_2O)_4]$ (M = Ba,Sr and M′ = Cu, Mn) systems: synthesis, structure, magnetic properties,and thermal decomposition. Inorg. Chem. **37** (1998) 3243–3251.
8. Wang, L. N.; Liu, X. R.; Wang, C. X.; Yan, L. Y.; Huang, J.: Preparation and thermal analysis of $C_{14}H_{10}N_4O_6$ and its complexes with rare earth. Synth. React. Inorg. Met.-Org. Chem. **39** (2009) 619–624.
9. Chen, Q. F.; Huang, F.; Quan, W. J.; Lu, Y. H.; Zhang, F.; Liu, F.: The crystal structure of hexaaqua(3-(3-(pyridin-4-yl)-1,2,4-oxadiazol-5-yl)propanoato-1κ^2*O,O*;2κ*O*′)(3-(3-(pyridin-4-yl)-1,2,4-odiazol-5-yl)propanoato-κ*O*)(3-(3-(pyridin-4-yl)-1,2,4-oxadiazol-5-yl)propanoato-κ^2*O,O*′)digadolinium(III) octahydrate, $C_{60}H_{76}Gd_2N_{18}O_{32}$. Z. Kristallogr. NCS **231** (2016) 457–460.
10. Zang, F.; Huang, F.; Zhang, Z. Q.; Yanhua Lu, Y. H.; Chen, Q. F.; Liu, F.: Crystal structure of hexaaqua-bis(3-(3-pyridin-4-yl-[1,2,4]oxadiazol-5-yl) propionato-κ^3*O*,*O*′:*O*′)-bis(3-(3-pyridin-4-yl-[1,2,4]oxadiazol-5-yl)propionato-κ*O*)-bis(3-(3pyridin-4-yl-[1,2,4]oxadiazol-5-yl)propionato-κ^2*O*,*O*′) dineodymium(III) octahydrate, $C_{60}H_{76}N_{18}O_{32}Nd_2$ Z. Kristallogr. NCS **231** (2016) 1135–1137.