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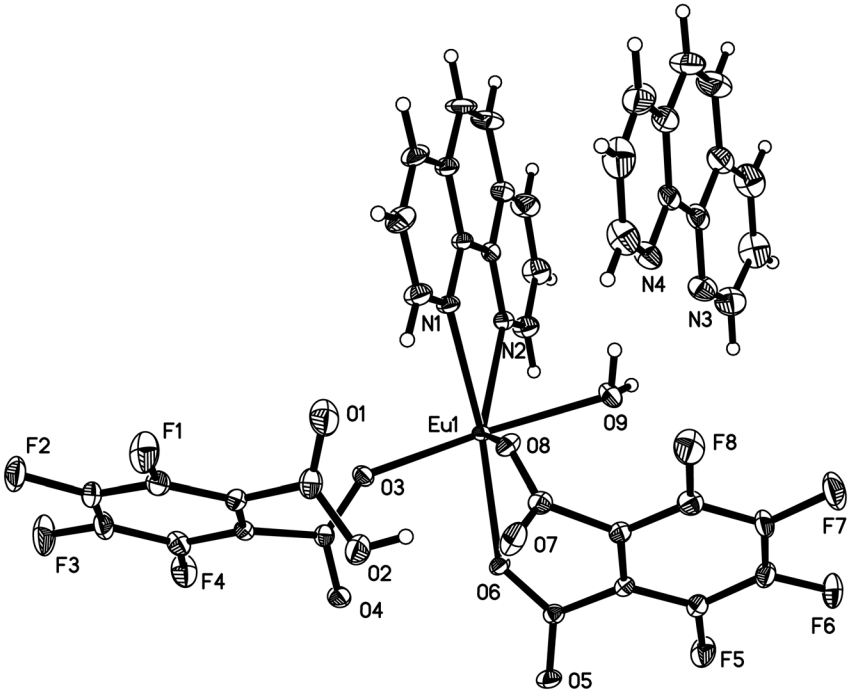
Crystal structure of diaqua-bis(μ_2-2-carboxy-3,4,5,6-tetrafluorobenzoato-κ^2*O*:*O*′)-bis(phenanthroline-κ^2*N*,*N*′)-bis(μ_2-3,4,5,6-tetrafluorophthalato-κ^3*O*:*O*,*O*′)dieuropium(III) – phenanthroline (1/2), $C_{40}H_{19}EuF_8N_4O_9$



https://doi.org/10.1515/ncrs-2022-0089
Received February 22, 2022; accepted May 9, 2022;
published online May 20, 2022

Abstract

$C_{40}H_{19}EuF_8N_4O_9$, triclinic, $P\bar{1}$ (no. 2), a = 11.3326(4) Å, b = 12.7652(4) Å, c = 13.2629(4) Å, α = 102.266(2)°, β = 97.689(2)°, γ = 105.630(3)°, V = 1767.93(10) Å^3, Z = 2, $R_{gt}(F)$ = 0.0329, $wR_{ref}(F^2)$ = 0.0648, T = 293(2) K.

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.19 × 0.18 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.88 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	29.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15,476, 8124, 0.036
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 7356
$N(param)_{refined}$:	561
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3, 4]

CCDC no.: 2153477

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Eu1	0.41561 (2)	0.83464 (2)	0.44811 (2)	0.01876 (5)
F1	0.46047 (18)	0.79923 (18)	0.99321 (15)	0.0493 (5)
F2	0.70361 (19)	0.87105 (17)	1.08322 (14)	0.0460 (5)
F3	0.86950 (19)	1.01006 (19)	1.00351 (17)	0.0581 (6)
F4	0.79489 (17)	1.07238 (17)	0.83285 (15)	0.0444 (5)
F5	0.17521 (18)	1.12051 (16)	0.31939 (15)	0.0432 (5)
F6	−0.04741 (18)	0.99019 (18)	0.20795 (14)	0.0452 (5)
F7	−0.17454 (18)	0.80717 (18)	0.26702 (16)	0.0535 (6)
F8	−0.06679 (18)	0.74943 (17)	0.43103 (17)	0.0501 (5)
O1	0.3065 (2)	0.7466 (2)	0.7838 (2)	0.0502 (7)
O2	0.3219 (2)	0.9269 (2)	0.78681 (18)	0.0407 (6)
H2	0.2585	0.9008	0.7403	0.061*
O3	0.49453 (19)	0.88944 (16)	0.63749 (15)	0.0252 (5)
O4	0.5758 (2)	1.07722 (17)	0.69839 (16)	0.0300 (5)
O5	0.3492 (2)	1.17246 (17)	0.50666 (17)	0.0322 (5)
O6	0.38206 (17)	1.01242 (16)	0.51217 (15)	0.0221 (4)
O7	0.1417 (2)	0.8916 (2)	0.63660 (17)	0.0390 (6)
O8	0.23770 (18)	0.80148 (17)	0.52914 (16)	0.0268 (5)
O9	0.22775 (19)	0.75510 (18)	0.31263 (16)	0.0321 (5)
H9A	0.1898	0.6823	0.3082	0.048*
H9B	0.2464	0.7512	0.2488	0.048*
N1	0.3694 (2)	0.63497 (19)	0.46945 (19)	0.0238 (5)
N2	0.4643 (2)	0.6908 (2)	0.30306 (19)	0.0250 (6)
C1	0.5858 (3)	0.9623 (2)	0.8163 (2)	0.0229 (6)
C2	0.4994 (3)	0.8915 (2)	0.8583 (2)	0.0245 (7)
C3	0.5413 (3)	0.8650 (3)	0.9493 (2)	0.0285 (7)
C4	0.6646 (3)	0.9028 (3)	0.9981 (2)	0.0317 (8)
C5	0.7484 (3)	0.9727 (3)	0.9584 (3)	0.0342 (8)
C6	0.7078 (3)	1.0036 (3)	0.8688 (2)	0.0286 (7)
C7	0.5471 (3)	0.9781 (2)	0.7070 (2)	0.0218 (6)
C8	0.3637 (3)	0.8447 (3)	0.8053 (2)	0.0302 (7)
C9	0.1773 (3)	1.0028 (2)	0.4353 (2)	0.0219 (6)
C10	0.1139 (3)	0.9047 (3)	0.4619 (2)	0.0235 (6)
C11	−0.0040 (3)	0.8430 (3)	0.4064 (3)	0.0299 (7)
C12	−0.0600 (3)	0.8717 (3)	0.3214 (2)	0.0321 (8)
C13	0.0022 (3)	0.9648 (3)	0.2933 (2)	0.0302 (7)
C14	0.1176 (3)	1.0302 (3)	0.3509 (2)	0.0270 (7)
C15	0.3093 (3)	1.0691 (2)	0.4884 (2)	0.0215 (6)
C16	0.1702 (3)	0.8630 (2)	0.5501 (2)	0.0253 (7)
C17	0.3238 (3)	0.6063 (3)	0.5500 (3)	0.0335 (8)
H17	0.3120	0.6623	0.6015	0.040*
C18	0.2925 (3)	0.4967 (3)	0.5619 (3)	0.0369 (8)
H18	0.2599	0.4808	0.6196	0.044*
C19	0.3101 (3)	0.4143 (3)	0.4888 (3)	0.0363 (8)
H19	0.2908	0.3412	0.4963	0.044*
C20	0.3813 (3)	0.3570 (3)	0.3217 (3)	0.0428 (9)
H20	0.3631	0.2828	0.3260	0.051*
C21	0.4289 (3)	0.3851 (3)	0.2418 (3)	0.0448 (10)
H21	0.4432	0.3298	0.1911	0.054*
C22	0.5131 (3)	0.5309 (3)	0.1499 (3)	0.0444 (9)
H22	0.5301	0.4783	0.0984	0.053*
C23	0.5408 (3)	0.6399 (3)	0.1465 (3)	0.0439 (9)
H23	0.5768	0.6627	0.0926	0.053*
C24	0.5151 (3)	0.7173 (3)	0.2241 (3)	0.0355 (8)
H24	0.5347	0.7918	0.2205	0.043*
C25	0.4374 (3)	0.5815 (2)	0.3077 (2)	0.0248 (7)
C26	0.3863 (3)	0.5513 (2)	0.3944 (2)	0.0237 (6)
C27	0.3575 (3)	0.4393 (3)	0.4019 (3)	0.0302 (7)
C28	0.4588 (3)	0.4978 (3)	0.2310 (2)	0.0326 (8)
N3	0.1721 (3)	0.6067 (2)	0.1003 (2)	0.0401 (7)
N4	0.0919 (3)	0.5328 (2)	0.2676 (2)	0.0404 (7)
C29	0.0470 (4)	0.4953 (4)	0.3439 (3)	0.0522 (10)
H29	0.0420	0.5479	0.4023	0.063*
C30	0.0064 (4)	0.3823 (4)	0.3430 (3)	0.0601 (12)
H30	−0.0270	0.3600	0.3982	0.072*
C31	0.0168 (4)	0.3055 (4)	0.2600 (4)	0.0560 (11)
H31	−0.0068	0.2295	0.2586	0.067*
C32	0.0727 (4)	0.2634 (3)	0.0852 (4)	0.0589 (12)
H32	0.0525	0.1872	0.0827	0.071*
C33	0.1101 (4)	0.2983 (3)	0.0034 (3)	0.0600 (12)
H33	0.1142	0.2459	−0.0555	0.072*
C34	0.1772 (4)	0.4547 (4)	−0.0818 (3)	0.0580 (12)
H34	0.1787	0.4042	−0.1431	0.070*
C35	0.2069 (4)	0.5661 (4)	−0.0758 (3)	0.0600 (12)
H35	0.2289	0.5933	−0.1327	0.072*
C36	0.2039 (4)	0.6390 (3)	0.0175 (3)	0.0506 (10)
H36	0.2259	0.7156	0.0215	0.061*
C37	0.1404 (3)	0.4954 (3)	0.0947 (3)	0.0340 (8)
C38	0.0991 (3)	0.4565 (3)	0.1818 (3)	0.0327 (8)
C39	0.0630 (3)	0.3407 (3)	0.1762 (3)	0.0419 (9)
C40	0.1438 (3)	0.4150 (3)	0.0047 (3)	0.0436 (9)

Source of material

A mixture of $Eu(NO_3)_3{\cdot}6H_2O$ (0.0893 g, 0.2 mmol), 3,4,5,6-tetrafluorophthalic acid (0.054 g, 0.2 mmol) and phenanthroline (35.7 mg, 0.15 mmol) were dissolved in 8 mL of deionized water. The mixture was sealed in a 25 mL Teflon-lined steel autoclave after ultrasound treatment for 15 min and heated at 110 °C for 72 h. The mixture was cooled to room temperature at a rate of 2 °C/h. Colorless block crystals were isolated by filtration, washed with distilled water and dried in air (CCDC number 2153477).

Experimental details

An empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was done [1].

Using Olex2 [2], the structure was solved with the ShelXT [3] structure solution program and refined with the ShelXL [4] refinement package.

The carbon bound hydrogen atoms were placed in calculated positions and refined using a riding model on attached atoms.

Comment

In recent decades, lanthanide complexes (Ln-CPs) have received particular attention because of their excellent luminescent properties such as high color purities, strong luminescence intensity, long lifetime and fast response time [5]. We are particularly interested in Eu-CPs because it can emit red fluorescence which is sensitive to naked eyes and can be used in multicolor displays and fluorescence probe [6, 7]. On the other hand, a perfluorinated multicarboxylate is an excellent ligand to construct Eu-CPs because it has a variety of coordination modes and can improve the luminescence properties of complexes [8, 9]. In addition, rigid N-containing ligands are versatile building blocks for luminescent materials and metal complexes [10–13]. In this work, a binuclear Eu-CP was constructed with 2,3,4,5-tetrafluorophthalic acid (TFPA) and phenanthroline as main and auxiliary ligand, respectively. Both ligands can improve the luminescence properties of Eu-CP by antenna effect.

The asymmetric unit of the title compound consists of one Eu(III) ion, one phen ligand, one tetrafluorophthalato (TFP) ligand, one 2-carboxy-3,4,5,6-tetrafluorobenzoate ligand (TFPH) one coordinated water molecule and one cocrystallized phen molecule. Each Eu(III) ion is nine-coordinated [$Eu_1O_7N_2$] by two N atoms of phen ligand, one O atoms from the coordinated water molecule and six O atoms from two TFP and two TFPH ligands. TFPH is mono-deprotonated and connected two adjacent Eu(III) cations with the carboxyl anion in mono coordination mode TFP is fully deprotonated and connected two adjacent Eu(III) cations in a chelating fashion (see the systematic name in the title). This coordination is different from similar lanthanide compound based on fluorine substituted ligands [8, 9]. The distances of Eu–O (carboxylate) and Eu–N range from 2.3900(19) to 2.683(2) and from 2.545(2) to 2.590(2) Å, respectively, and the distance of Eu–O (water) is 2.414(2) Å, which are consistent with the values for reported Eu(III) complexes [14, 15]. The carboxylate groups from TFP and TFPH form four bridges and link two adjacent Eu(III) cations, resulting in the dinuclear units with Eu···Eu separation of just 3.9813(2) Å. The cocrystallized phen molecules are linked to the {Eu_2} dinuclear units via O–H··· N hydrogen bonds. The dinuclear units are further connected into a three dimensional supramolecular structure via C–H···O hydrogen bonds and π–π interactions.

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

Research funding: This work was supported by the Training Program for Young Cadre Teachers of Higher Education Institutions in Henan Province (No. 2018GGJS128) and Science and Technology Development Project in Henan Province (No. 172101410037).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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