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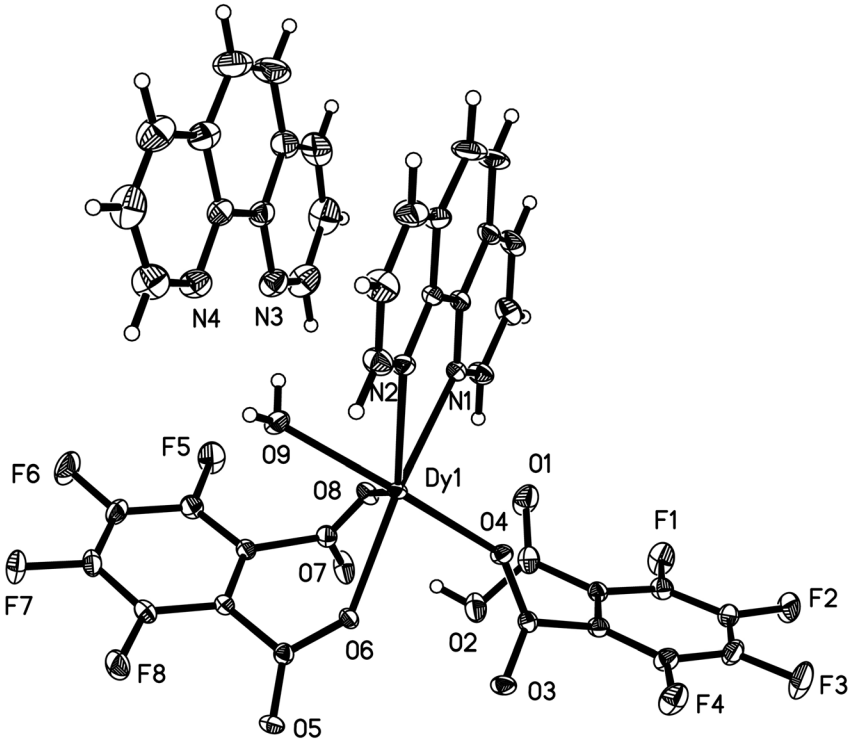
Crystal structure of diaqua-diphenanthroline-κ^2*N,N′*-bis(μ_2-2-carboxy-3,4,5,6-tetrafluorobenzoato-κ^2*O:O′*)-bis(μ_2-tetrafluorophthalato-κ^3*O,O′:O′*)didysprosium(III) – phenanthroline (1/2), $C_{80}H_{38}Dy_2F_{16}N_8O_{18}$



https://doi.org/10.1515/ncrs-2022-0289
Received June 13, 2022; accepted June 13, 2022;
published online August 11, 2022

Abstract

$C_{80}H_{38}Dy_2F_{16}N_8O_{18}$, triclinic, $P\bar{1}$ (no. 2), a = 11.3924(5) Å, b = 12.7091(4) Å, c = 13.2583(5) Å, α = 102.496(3)°, β = 97.955(4)°, γ = 105.588(4)°, V = 1765.36(12) Å^3, Z = 2, $R_{gt}(F)$ = 0.0298, $wR_{ref}(F^2)$ = 0.0606, T = 293(2) K.

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CCDC no.: 2153477

The asymmetric unit of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.19 × 0.18 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	2.23 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	29.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16224, 8196, 0.028
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7557
$N(param)_{refined}$:	565
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3, 4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Dy1	0.41528 (2)	0.83634 (2)	0.44862 (2)	0.01792 (4)
F1	0.46272 (19)	0.80107 (17)	0.99306 (14)	0.0465 (5)
F2	0.70525 (19)	0.87111 (17)	1.08137 (14)	0.0451 (5)
F3	0.87048 (19)	1.00941 (19)	1.00099 (16)	0.0557 (6)
F4	0.79487 (18)	1.07260 (16)	0.83104 (14)	0.0428 (5)
F5	−0.06548 (18)	0.75199 (17)	0.43227 (16)	0.0489 (5)
F6	−0.17347 (19)	0.80968 (18)	0.26804 (16)	0.0525 (6)
F7	−0.04658 (19)	0.99209 (17)	0.20819 (14)	0.0434 (5)
F8	0.17727 (19)	1.12230 (16)	0.31852 (15)	0.0421 (5)
O1	0.3060 (2)	0.7478 (2)	0.78460 (19)	0.0479 (7)
O2	0.3239 (2)	0.9289 (2)	0.78652 (18)	0.0401 (6)
H2	0.2597	0.9024	0.7407	0.060*
O3	0.5768 (2)	1.07762 (16)	0.69644 (15)	0.0285 (5)
O4	0.49264 (19)	0.88821 (16)	0.63512 (14)	0.0238 (4)
O5	0.3519 (2)	1.17454 (16)	0.50476 (16)	0.0317 (5)
O6	0.38412 (18)	1.01348 (15)	0.51152 (14)	0.0210 (4)
O7	0.1425 (2)	0.8920 (2)	0.63637 (17)	0.0390 (6)
O8	0.24177 (19)	0.80514 (16)	0.52977 (15)	0.0258 (5)
O9	0.2311 (2)	0.7562 (2)	0.31571 (17)	0.0302 (5)
H9A	0.2473	0.7649	0.2553	0.045*
H9B	0.195 (4)	0.691 (4)	0.302 (3)	0.072 (15)*
N1	0.3704 (2)	0.63910 (19)	0.46976 (18)	0.0228 (5)
N2	0.4657 (2)	0.69544 (19)	0.30468 (18)	0.0240 (5)
C1	0.5001 (3)	0.8921 (2)	0.8576 (2)	0.0228 (6)
C2	0.5856 (3)	0.9620 (2)	0.8146 (2)	0.0233 (6)
C3	0.7076 (3)	1.0038 (3)	0.8668 (2)	0.0283 (7)
C4	0.7498 (3)	0.9734 (3)	0.9561 (2)	0.0325 (7)
C5	0.6662 (3)	0.9033 (3)	0.9967 (2)	0.0300 (7)
C6	0.5427 (3)	0.8659 (3)	0.9483 (2)	0.0275 (7)
C7	0.3651 (3)	0.8467 (3)	0.8053 (2)	0.0307 (7)
C8	0.5470 (3)	0.9779 (2)	0.7057 (2)	0.0214 (6)
C9	0.1800 (3)	1.0041 (2)	0.4349 (2)	0.0206 (6)
C10	0.1159 (3)	0.9065 (2)	0.4622 (2)	0.0220 (6)
C11	−0.0025 (3)	0.8454 (3)	0.4068 (2)	0.0295 (7)
C12	−0.0587 (3)	0.8733 (3)	0.3226 (2)	0.0317 (7)
C13	0.0038 (3)	0.9665 (3)	0.2934 (2)	0.0300 (7)
C14	0.1197 (3)	1.0325 (2)	0.3513 (2)	0.0262 (7)
C15	0.3120 (3)	1.0710 (2)	0.4878 (2)	0.0212 (6)
C16	0.1728 (3)	0.8648 (2)	0.5503 (2)	0.0236 (6)
C17	0.3245 (3)	0.6110 (3)	0.5504 (2)	0.0308 (7)
H17	0.3120	0.6672	0.6017	0.037*
C18	0.2941 (3)	0.5006 (3)	0.5618 (3)	0.0366 (8)
H18	0.2632	0.4849	0.6200	0.044*
C19	0.3099 (3)	0.4170 (3)	0.4879 (3)	0.0365 (8)
H19	0.2883	0.3431	0.4941	0.044*
C20	0.3815 (4)	0.3593 (3)	0.3211 (3)	0.0435 (9)
H20	0.3621	0.2845	0.3247	0.052*
C21	0.4299 (4)	0.3876 (3)	0.2411 (3)	0.0448 (9)
H21	0.4447	0.3323	0.1905	0.054*
C22	0.5141 (4)	0.5346 (3)	0.1501 (3)	0.0432 (9)
H22	0.5305	0.4817	0.0981	0.052*
C23	0.5430 (4)	0.6446 (3)	0.1480 (3)	0.0434 (9)
H23	0.5801	0.6679	0.0951	0.052*
C24	0.5165 (3)	0.7226 (3)	0.2259 (2)	0.0345 (8)
H24	0.5353	0.7974	0.2225	0.041*
C25	0.4382 (3)	0.5855 (2)	0.3080 (2)	0.0234 (6)
C26	0.4593 (3)	0.5008 (3)	0.2315 (2)	0.0323 (7)
C27	0.3590 (3)	0.4424 (2)	0.4016 (2)	0.0287 (7)
C28	0.3870 (3)	0.5553 (2)	0.3954 (2)	0.0238 (6)
N3	0.0923 (3)	0.5343 (2)	0.2690 (2)	0.0396 (7)
N4	0.1733 (3)	0.6083 (2)	0.1020 (2)	0.0408 (7)
C29	0.0460 (4)	0.4962 (4)	0.3450 (3)	0.0527 (10)
H29	0.0407	0.5487	0.4037	0.063*
C30	0.0049 (4)	0.3818 (4)	0.3422 (3)	0.0594 (12)
H30	−0.0292	0.3590	0.3967	0.071*
C31	0.0153 (4)	0.3045 (3)	0.2589 (3)	0.0549 (11)
H31	−0.0091	0.2279	0.2567	0.066*
C32	0.0724 (4)	0.2629 (3)	0.0846 (4)	0.0601 (12)
H32	0.0524	0.1862	0.0818	0.072*
C33	0.1095 (4)	0.2977 (3)	0.0027 (3)	0.0611 (12)
H33	0.1133	0.2448	−0.0564	0.073*
C34	0.1778 (4)	0.4554 (4)	−0.0808 (3)	0.0575 (11)
H34	0.1797	0.4047	−0.1422	0.069*
C35	0.2082 (4)	0.5668 (4)	−0.0744 (3)	0.0596 (12)
H35	0.2307	0.5939	−0.1310	0.071*
C36	0.2052 (4)	0.6407 (3)	0.0190 (3)	0.0520 (10)
H36	0.2272	0.7177	0.0230	0.062*
C37	0.1410 (3)	0.4959 (3)	0.0952 (3)	0.0348 (8)
C38	0.1433 (4)	0.4154 (3)	0.0046 (3)	0.0449 (9)
C39	0.0630 (3)	0.3401 (3)	0.1756 (3)	0.0428 (9)
C40	0.0989 (3)	0.4570 (3)	0.1827 (3)	0.0338 (7)

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

Source of materials

$Dy(NO_3)_3{\cdot}6H_2O$ (0.0913 g, 0.2 mmol), 3,4,5,6-tetrafluorophthalate (0.054 g, 0.2 mmol) and phenanthroline (35.7 mg, 0.15 mmol) were mixed with 8 mL of deionized water in a reagent bottle. The mixture was treated by ultrasonic waves for 15 min at room temperature, sealed in a 25 mL Teflon-lined steel autoclave and heated at 110 °C for 72 h. The mixture was cooled to room temperature within 36 h and colorless block crystals were isolated after filtration, washed with distilled water and dried in air.

Experimental details

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 the last decades, a large number of Dy(III)-metal organic frameworks (MOFs) have been reported due to their excellent magnetic and optical properties [5–7]. Dy–MOFs can be constructed from Dy(III) ion and carboxylate and nitrogen-containing ligands [8–10]. Among various carboxylate ligands, tetrafluorophthalate (TFPA) is a good candidate because it has multiple coordinate modes and can serve as a bridging ligand [11–13]. In addition, phenanthroline (phen) is one of the commonly used N-containing ligands in combination with carboxylates [14, 15]. In this work, a binuclear Dy–complex was constructed with TFPA and phen as ligands. It is worth noting that, using the same reactants as described in the literature, different framework structures are produced due to different reaction conditions [9, 10]. Thus the dinuclear title complex was obtained unexpectedly.

In the title complex, there are one Dy(III) ion, one phen ligand, two differently deprotonated tetrafluorophthalato ligands ($HTFPA^-$ and $TFPA^{2-}$, respectively), one coordinated water and one cocrystallized phen in the asymmetric unit. The cocrystallized phen molecule is linked to the coordinated water by a hydrogen bond (O9–H9A···N3). Dy1 is nine-coordinated by two N atoms (N1, N2) of the phen ligand, one O atom (O9) from coordinated water, two O atoms (O4, O3A) from two mono-deprotonated $HTFPA^-$ ligands and four O atoms (O6, O8, O5A and O6A) from two fully-deprotonated $TFPA^{2-}$ ligands. The Dy–N bond lengths are 2.506(2) and 2.561(2) Å and the Dy–O ones are in the range of 2.0560(14)–2.3610(19) Å. Two Dy(III) ions are bridged by two $HTFPA^-$ and two $TFPA^{2-}$ ligands to form a dinuclear $\{Dy_2\}$ unit, which is further connected into a 3D structure by π–π interactions and C–H···O hydrogen bonds.

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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