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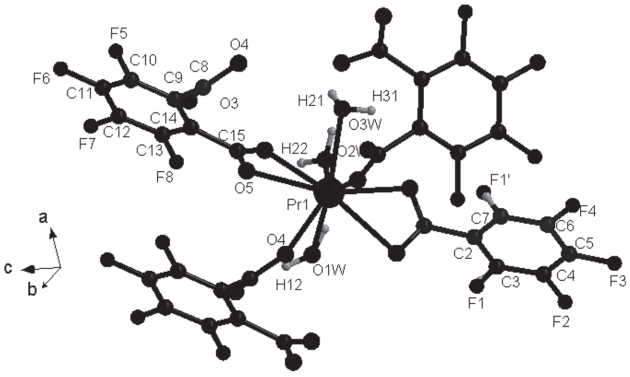
Crystal structure of *poly*-[triaqua-(μ_3-3,4,5,6-tetrafluoro-1,2-phthalato-$\kappa^4O:O':O'',O'''$) (2,3,4,5-tetrafluoro-benzoato-κ^2O,O') praseodymium(III)], $C_{15}H_7F_8O_9Pr$



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Abstract

$C_{15}H_7F_8O_9Pr$, monoclinic, $P2_1/n$ (no. 14), $a = 6.2167(3)$ Å, $b = 9.7769(5)$ Å, $c = 29.6562(15)$ Å, $\beta = 93.2916(8)°$, $V = 1799.53$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0317$, $wR_{ref}(F^2) = 0.0729$, $T = 293(2)$ K.

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The asymmetric unit of the crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

3,4,5,6-Tetrafluorobenzene-1,2-dioic acid, (Tfpa, 0.048 g, 0.2 mmol) and sodium formate dihydrate (0.020 g,

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Table 1: Data collection and handling.

Crystal:	Yellow rodlike
	Size 0.26 × 0.21 × 0.17 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	28.4 cm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω
$2\theta_{max}$, completeness:	55.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8978, 3170, 0.027
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2993
$N(param)_{refined}$:	313
Programs:	SHELX [12], Bruker programs [13]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Pr1	0.4537(1)	0.9479(1)	0.7049(1)	0.01757(10)
F1[a]	−0.2035(8)	0.7821(7)	0.5999(2)	0.0299(14)
F2	−0.3660(6)	0.7145(4)	0.5200(1)	0.0558(10)
F3	−0.1458(7)	0.7637(4)	0.4456(1)	0.0623(12)
F4	0.2514(7)	0.8769(4)	0.4541(1)	0.0580(11)
F1'[a]	0.4085(13)	0.9558(9)	0.5330(3)	0.060(2)
F5	0.1223(5)	0.6126(3)	0.6305(1)	0.0357(8)
F6	0.2551(6)	0.5328(4)	0.5495(1)	0.0493(9)
F7	0.6501(6)	0.4138(4)	0.5442(1)	0.0483(9)
F8	0.8993(5)	0.3658(3)	0.6193(1)	0.0385(8)
O1	0.4201(6)	0.9110(5)	0.6221(1)	0.0453(11)
O2	0.1047(6)	0.9298(4)	0.6506(1)	0.0306(8)
O3	0.3286(6)	0.7102(3)	0.7164(1)	0.0255(8)
O4	0.3168(5)	0.4931(4)	0.7392(1)	0.0257(8)
O5	0.8235(6)	0.5589(4)	0.7317(1)	0.0269(8)
O6	0.8861(6)	0.3432(4)	0.7152(1)	0.0316(8)
O1W	0.3227(7)	1.1922(4)	0.6929(2)	0.0414(10)
H12	0.410(4)	1.137(5)	0.683(2)	0.05000*
H11	0.300(12)	1.227(7)	0.7176(13)	0.06200*
O2W	0.7370(6)	1.0976(4)	0.6712(1)	0.0349(9)
H21	0.8440	1.0497	0.6653	0.05200*
H22	0.7820	1.1695	0.6841	0.05200*
O3W	0.7754(6)	0.8084(4)	0.6952(1)	0.0341(9)
H31	0.8880	0.8548	0.6930	0.05100*
H32	0.7352	0.7816	0.6691	0.05100*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C1	0.2189(8)	0.9069(5)	0.6172(2)	0.0252(11)
C2	0.1175(8)	0.8716(5)	0.5719(2)	0.0256(11)
C3	−0.0867(9)	0.8123(6)	0.5666(2)	0.0306(12)
H3[a]	−0.1666	0.7984	0.5918	0.03700*
C4	−0.1702(9)	0.7745(6)	0.5246(2)	0.0361(14)
C5	−0.0583(11)	0.7958(6)	0.4867(2)	0.0391(14)
C6	0.1443(10)	0.8539(6)	0.4914(2)	0.0376(14)
C7	0.2305(9)	0.8917(6)	0.5332(2)	0.0314(12)
H7[a]	0.3666	0.9314	0.5358	0.03800*
C8	0.3589(7)	0.5856(5)	0.7117(2)	0.0197(10)
C9	0.4468(7)	0.5366(5)	0.6674(2)	0.0194(10)
C10	0.3190(8)	0.5552(5)	0.6284(2)	0.0263(11)
C11	0.3817(9)	0.5127(6)	0.5866(2)	0.0315(12)
C12	0.5813(10)	0.4500(6)	0.5843(2)	0.0322(12)
C13	0.7076(8)	0.4274(5)	0.6232(2)	0.0253(11)
C14	0.6465(7)	0.4718(5)	0.6651(2)	0.0199(10)
C15	0.7963(7)	0.4548(5)	0.7066(2)	0.0206(10)

[a]Occupancy: 0.50.

0.15 mmol) in a solution of water/alcohol (v/v = 1.5, 10 mL) were mixed with an aqueous solution (10 mL) praseodymium(III) nitrate hexahydrate (0.041 g, 0.2 mmol). After stirring for 20 min in air, the pH value was adjusted to 3.0 with nitric acid, and the mixture was placed into a 25 mL Teflon-lined autoclave under autogenous pressure being heated at 145 °C for 72 h, then cooled at 5 °C/h. After filtration, the product was washed with distilled water and dried. Yellow crystals of the title compound were obtained. Yield: 0.0481 g (39%) based on Pr. **Elemental analysis** (%): calc for C_{15} H_7 F_8 O_9Pr: C 28.87, H 1.13, found: C 29.23, H 1.19. **IR** (KBr pellet, c^{-1}): 3343 s, 2178 s, 1626 s, 1559 s, 1428 s, 1309 s, 1112 s, 866 m, 793 s, 660 s, 519 s.

Experimental details

Positions of hydrogen atoms of the water molecules were located from the difference Fourier maps and refined. All U_{iso} values were restrained on U_{eq} values of the parent atoms.

Discussion

The design and construction of lanthanide-metal-organic frameworks (Ln—MOFs) based on the judicious selection of ligands and metal ions have become a very attractive research field of coordination chemistry and crystal engineering [1, 2]. This contributes to their potential application in areas of luminescent probe, catalysis, gas storage, nonlinear optics, magnetism [3, 4]. Lanthanide coordination polymers based on polycarboxylic ligands are prevalent because of their high structural stability and various coordination modes [5, 6]. The addition of completely or partially deprotonated carboxylate groups on the molecules is beneficial to the formation of unusual multidimensional architectures [7]. The luminescence intensity is often quenched by the non-radiative exchange of electronic energy of Ln(III) to the high vibration modes of O—H, C—H bonding in ligands [8], in order to avoid deactivation processes, the role of the carboxylic ligand is to shield lanthanide center against the solvent [8]. The introduction of fluoro atoms in ligands reduces convert O—H, C—H bond number, thereby enhancing the fluorescence quantum efficiency and extending the fluorescence lifetime. In this paper, the rigid ligand 3,4,5,6-tetrafluoro-1,2 phthalate was employed. As illustrated in the figure, the asymmetric unit of title compound contains one Pr(III) cation, one Tfpa anion and 2,3,4,5 tetrafluoro-benzoate ligand, which is generated from starting materials of Tfpa, as well as three water molecules. The Pr(III) is coordinated by nine oxygen atoms, and the coordintion polyhedron around the central ion is best described as distored a monocapped anti-prism. Six oxygen atoms are from the carboxylate moieties. The other three oxygen atoms are from water molecules Tfpa exhibits both chelating and bridging modes linking two adjacent Pr(III) ions, while the benzoato ligand uses the carboxylate group in chelating coordination fashion. Obviously, this is different from the analogous praseodymium (III) complex based on the ligand of 2,6-bis(phenylhydrazone)pyridine, in which the central ion exhibits distorted bicapped square antiprism geometry, In addition to the three anionic oxygen, Pr(III) complete their coordination spheres with six neutral nitrogen from the ligand molecules and one neutral oxygen around the central ion [9], nor is comparble to the Pr(III) complex with the pentadentate dianionic Schiff base ligand, H_2L [N1,N3-bis(salicylideneimino)diethylenetriamine], Schiff base ligand exhibits a N_3O_2 donor set [10]. The Pr—O distances range from 2.451(4) to 2.719(4) Å, which are consistent with other Pr(III) complex reported previously [11]. The bond angles at Pr(III) are in the range of 71.68(12) to 160.97(13)°. The carboxylate groups of Tfpa adopt two different types of coordination modes. The dihedral angles between phenyl ring and Pr—O—O—C plane within the same Tfpa ligand is 25.59°, indicating the carboxyl group is distorted from the plane of benzene ring at some extend, while the dihedral angles between two phenyl rings sharing the common Pr (III) ion is 50.22°. These dinuclear units mentioned before are further interconnected and extended through terminal oxygen atoms from carboxylate into a 1D zigzag chain array. These chains are further interconnected through another carboxylate oxygen atoms into complicated two dimensional coordination networks consequently. A close inspection reveals the seperation between adjacent phenyl rings within 2D sheet just about 3.3 Å, indicating there prescence strong π-π stacking between layers.

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