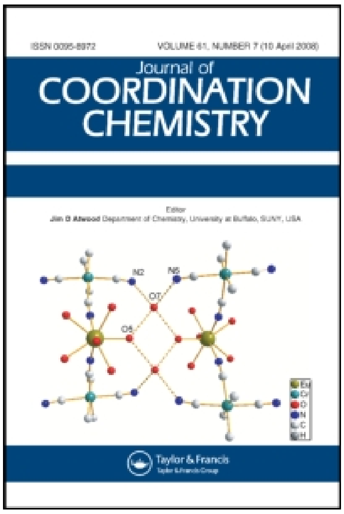

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The first terbium(III) complex of 5-fluorouracil-1-acetic acid, a new 2D coordination polymer, $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$, phen = 1,10-phenanthroline and 5-FUA = 5-fluorouracil-1-acetate

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A new Tb^{III} complex of 5-fluorouracil-1-acetate (5-FUA) and 1,10-phenanthroline(phen), $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$, has been synthesized, characterized by elemental analysis, IR spectroscopy, XRD powder diffraction, thermal analysis and its structure has been determined by X-ray crystallography. The structural studies show that compound to be a two-dimensional coordination polymer and the Tb atoms to have ten-coordinate geometry, TbN_2O_8. Self-assembly of this compound in the solid state is likely caused by N–H···O, O–H···O and O–H···F hydrogen bonding.

Keywords: Terbium(III); 5-Fluorouracil-1-acetate; 1,10-Phenanthroline, Hydrogen bonding; Coordination polymer

1. Introduction

5-Fluorouracil is an antimetabolite with good antimicrobial and antitumor activity, but its administration is accompanied by significant toxic side effects and delivery problems [1–5]. In order to improve the topical delivery of 5-fluorouracil and reduce the side effects, many derivatives of 5-fluorouracil have been synthesized, some of which have better biological activity. 5-fluorouracil-1-acetic acid is a member of the family. It is of interest to us that 5-FUA anion with both carboxylate and carbonyl as potential coordinating groups, can form not only a short-bridge via one carboxylate but also a long-bridge via the central uracil ring between metal ions [6–10]. To our knowledge, only a few transition metal complexes with "5-FUA" have been reported. To extend this research, we report here the hydrothermal synthesis and structural characterization

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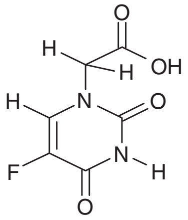
of a Tb^{3+} complex of 5-FUA and phen, $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$, the first rare earth complexe of 5-FUA.



5-Fluorouracil-1-acetic acid

2. Experimental

2.1. *Preparation of [Tb(phen)(5-FUA)$_3$]$_n$ · H$_2$O*

The title compound was synthesized in a hydrothermal process from a mixture of 1,10-phenanthroline (2 mmol, 0.36 g), $Tb(ClO_4)_3 \cdot 6H_2O$ (1 mmol, 0.57 g), 5-fluorouracil-1-acetic acid (2 mmol, 0.38 g) and water (20 mL). The reaction was carried out in a 30 mL Teflon-lined, stainless-steel reactor heated to 436 K for four days. The reactor was slowly cooled to room temperature to yield colorless crystals that were collected and washed with distilled water. The yield is ca 68% based on Tb(III). The substance is insoluble in water and common organic solvents. (m.p. = 257°C). Yield: 0.25 g, 50%. $C_{30}H_{22}F_3N_8O_{13}Tb$: Calcd C, 39.20; H, 2.40; N, 12.19; Found C, 38.91; H, 2.61; N, 11.98%. -IR (KBr, cm^{-1}) selected bonds: $\nu = 768$(m), 724(m), 8021(w), 899(w), 984(w), 1202(w), 1371(vs), 1490(s), 1564(s), 1581(s), 1667(s), 2858(s), 3025(w), 3212(b).

2.2. *Crystallography*

Crystallographic measurements were made at 298(2) K using a Bruker APEX area-detector diffractometer. The intensity data were collected within the range 1.92 to 25.25° using graphite monochromated Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2. Structure solution and refinement were accomplished using SIR97, SHELXL97 and WinGX [11–12].

Crystal data and structure refinement parameters are given in table 1. Selected bond lengths and angles are given in table 2. Anisotropic thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. An ORTEP diagram and perspective views of the packing are shown in figures 1–2.

2.3. *XRD powder diffraction and thermal analysis*

XRD Powder sample of the bulk sample synthesized was assessed by a Siemens D5000 X-ray powder diffractometer (Hamburg, Germany) using Cu-Kα radiation generated at 40 kV and 30 mA, with an angular increment of 0.05°C. To access the thermal stability of the title compound, TGA analyses were carried out on a NETZSCH STA 449C unit, at a heating rate of 15°C min^{-1} under a nitrogen atmosphere.

Table 1. Crystal data and structure refinement for $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$.

Identification code	$[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$
Empirical formula	$C_{30}H_{22}F_3N_8O_{13}Tb$
Formula weight	918.48
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*P*21/c
Unit cell dimensions (Å, °)	
a	15.084(5)
b	17.211(5)
c	14.151(4)
β	116.946(4)
Volume (Å^3)	3274.9(17)
Z	4
Density (calculated) (Mg m^{-3})	1.863
Absorption coefficient (mm^{-1})	0.806
F(000)	1816
Crystal size (mm^3)	0.32 × 0.26 × 0.24
θ range for data collection (°)	1.92–25.25
Index ranges	$-18 \le h \le 15$, $-14 \le k \le 20$, $-15 \le l \le 16$
Reflections collected	17115
Independent reflections	5887 [R(int) = 0.0438]
Completeness to theta	99.1%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5832 and 0.5018
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5887/0/496
Goodness-of-fit on F^2	1.043
Final R [$I > 2\sigma(I)$]	Indices for 5887 ref. [1] $R_1 = 0.0604$, $wR_2 = 0.1587$
R indices (all data)	$R_1 = 0.0796$, $wR_2 = 0.1644$
Largest diff. Peak, hole (e Å^{-3})	0.653 and −1.654

3. Results and discussion

Reaction between 1,10-phenanthroline (phen) and a mixture of terbium(III) perchlorate with 5-fluorouracil-1-acetic acid provided crystalline materials analyzing as $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$. The IR spectrum displays characteristic absorption bands for "phen", water ligands and 5-FUA anions. The relatively weak absorption bands around 2858 and 3025 cm^{-1} are due to the C–H modes involving the aliphatic and aromatic hydrogen atoms, respectively. The characteristic bands of the carboxylate groups appear at 1371 υ_{as}(C–O) and 1581 υ_{sym}(C–O) cm^{-1}. Three strong band at 1667 cm^{-1} characterizes the ν(C=O) vibrations. The absorption bands with variable intensity in the frequency range 1400–1590 cm^{-1} correspond to ring vibrations of "ph" moiety of the "phen" ligand. The broad absorption band for ν(HOH) at 3100–3250 cm^{-1} indicates the presence of water molecules, attributable to ν(O–H$\cdots$X), indicating the presence of hydrogen bonds, which is confirmed by the crystal structure of this complex.

Results of XRD powder patterns indicate that the experimental data are in good agreement with the simulated XRD powder patterns based on single crystal data, hence $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$ is obtained as a mono-phase.

Table 2. Bond lengths(Å) and angles(°) for [Tb(phen)(5-FUA)$_3$]$_n \cdot$ H$_2$O.

Tb(1)–O(10)^{i}	2.506(5)
Tb(1)–O(1)	2.535(5)
Tb(1)–O(5)	2.573(5)
Tb(1)–O(2)^{ii}	2.578(5)
Tb(1)–O(9)^{iii}	2.594(5)
Tb(1)–O(12)	2.621(5)
Tb(1)–N(1)	2.689(5)
Tb(1)–N(2)	2.717(6)
Tb(1)–O(10)^{iii}	2.799(5)
Tb(1)–O(6)	2.841(6)
O(10)^{i}–Tb(1)–O(1)	74.15(16)
O(10)^{i}–Tb(1)–O(5)	70.84(15)
O(1)–Tb(1)–O(5)	135.99(17)
O(10)^{i}–Tb(1)–O(2)^{ii}	73.90(15)
O(1)–Tb(1)–O(2)^{ii}	127.34(16)
O(5)–Tb(1)–O(2)^{ii}	65.91(17)
O(10)^{i}–Tb(1)–O(9)^{iii}	117.26(14)
O(1)–Tb(1)–O(9)^{iii}	76.19(16)
O(5)–Tb(1)–O(9)^{iii}	144.56(17)
O(2)^{ii}–Tb(1)–O(9)^{iii}	82.75(16)
O(10)^{i}–Tb(1)–O(12)	144.23(15)
O(1)–Tb(1)–O(12)	137.06(16)
O(5)–Tb(1)–O(12)	85.73(16)
O(2)^{ii}–Tb(1)–O(12)	71.92(15)
O(9)^{iii}–Tb(1)–O(12)	68.41(15)
O(10)^{i}–Tb(1)–N(1)	86.98(16)
O(1)–Tb(1)–N(1)	68.12(17)
O(5)–Tb(1)–N(1)	84.08(18)
O(2)^{ii}–Tb(1)–N(1)	148.22(17)
O(9)^{iii}–Tb(1)–N(1)	128.95(17)
O(12)–Tb(1)–N(1)	117.87(16)
O(10)^{i}–Tb(1)–N(2)	143.91(16)
O(1)–Tb(1)–N(2)	78.38(16)
O(5)–Tb(1)–N(2)	117.71(17)
O(2)^{ii}–Tb(1)–N(2)	142.18(16)
O(9)^{iii}–Tb(1)–N(2)	77.29(17)
O(12)–Tb(1)–N(2)	70.94(16)
N(1)–Tb(1)–N(2)	60.99(18)
O(10)^{i}–Tb(1)–O(10)^{iii}	69.68(16)
O(1)–Tb(1)–O(10)^{iii}	63.81(15)
O(5)–Tb(1)–O(10)^{iii}	124.18(15)
O(2)^{ii}–Tb(1)–O(10)^{iii}	66.30(15)
O(9)^{iii}–Tb(1)–O(10)^{iii}	47.64(14)
O(12)–Tb(1)–O(10)^{iii}	105.11(15)
N(1)–Tb(1)–O(10)^{iii}	130.53(15)
N(2)–Tb(1)–O(10)^{iii}	117.57(16)
O(10)^{i}–Tb(1)–O(6)	112.13(17)
O(1)–Tb(1)–O(6)	132.42(17)
O(5)–Tb(1)–O(6)	47.00(17)
O(2)^{ii}–Tb(1)–O(6)	98.26(17)
O(9)^{iii}–Tb(1)–O(6)	128.61(17)
O(12)–Tb(1)–O(6)	63.46(17)
N(1)–Tb(1)–O(6)	65.33(17)
N(2)–Tb(1)–O(6)	71.16(18)
O(10)^{iii}–Tb(1)–O(6)	163.77(16)

(i) $-x+1,\ y-1/2,\ -z+3/2$; (ii) $-x+1,\ -y+1,\ -z+1$; (iii) $x,\ -y+3/2,\ z-1/2$.

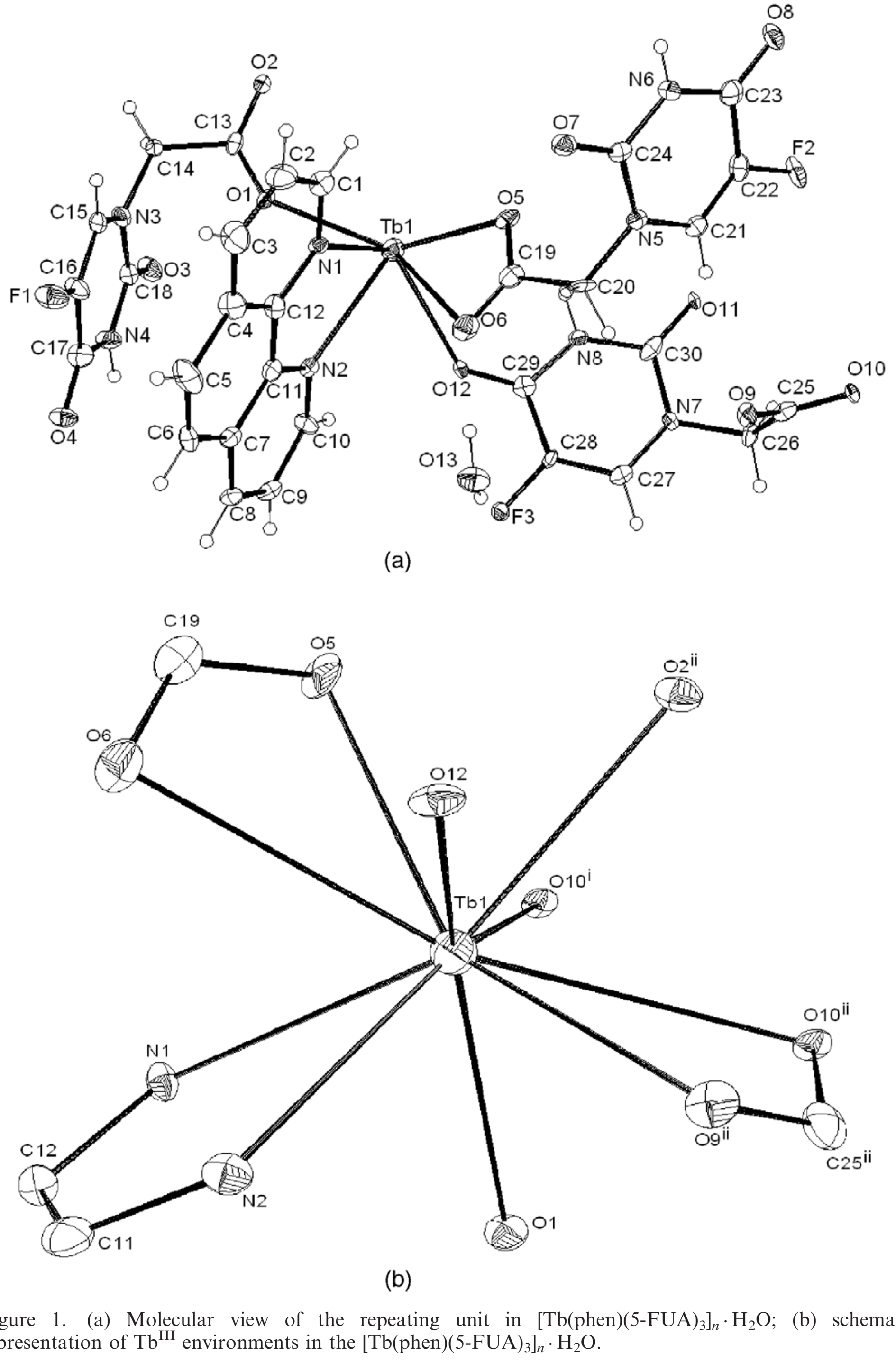


Figure 1. (a) Molecular view of the repeating unit in $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$; (b) schematic representation of Tb^{III} environments in the $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$.

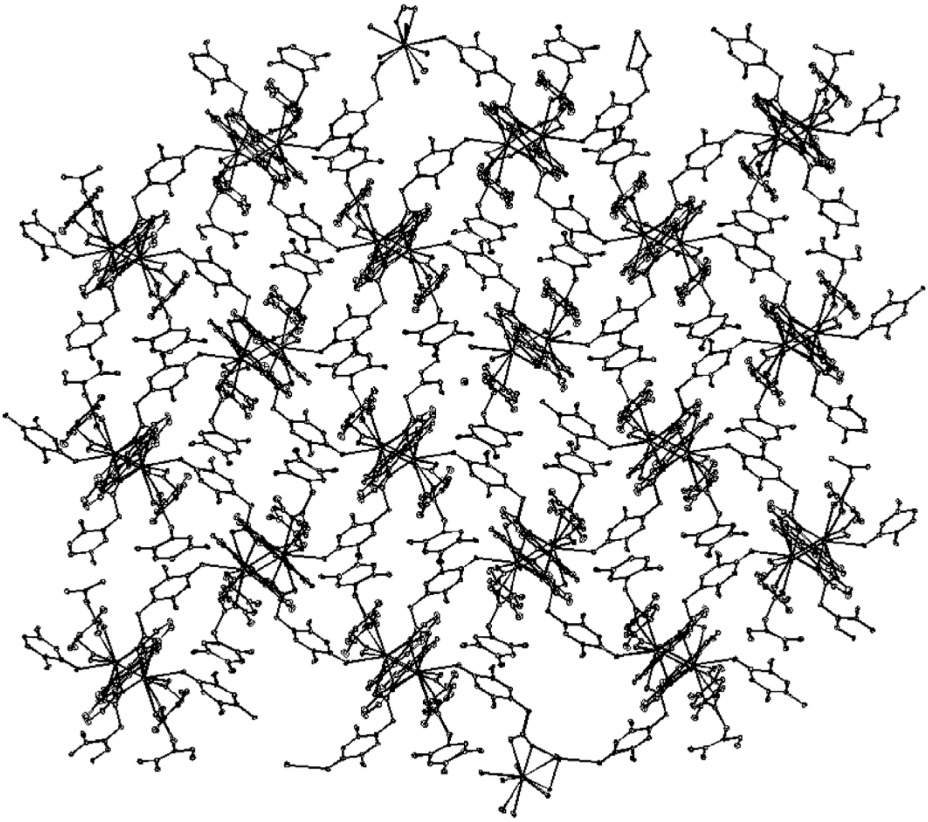
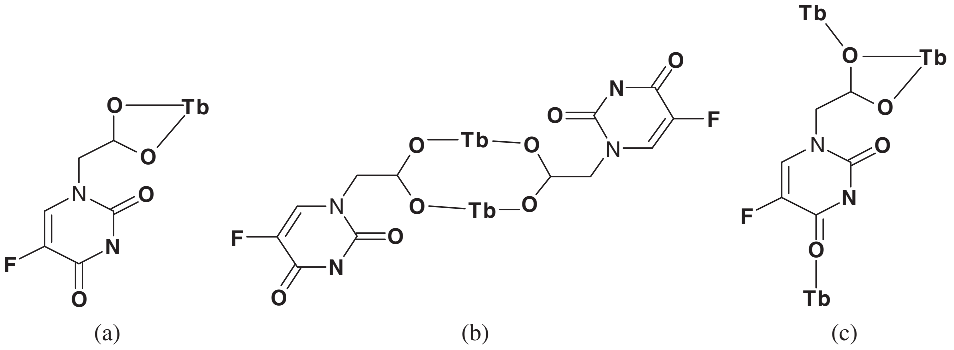


Figure 2. A packing diagram showing the two-dimensional polymer in $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$.

Results of TGA show two main weight losses. $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$ is stable up to 115°C with weight loss of 2.13% occurring from 115°C to 160°C from release of water (calculated value, 1.96%). The second weight loss appeared from 417°C to 784°C, during which the compound is decomposed. The final product is Tb_2O_3. The total weight loss of 79.84% is close to the calculated value of 80.08%.

Determination of the structure of $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$ by X-ray crystallography (table 1) showed the compound to be a two-dimensional polymer (figures 1 and 2). The terbium atoms are linked by oxygen atoms of "5-FUA" anions and can be considered to be ten-coordinate with O_8N_2 coordination. The terbium atoms are linked by eight oxygens of three different "5-FUA" anions with Tb–O distance rang at 2.50–2.80 Å and two nitrogen atoms of phen with distances of Tb(1)–N(1) = 2.689(5) and Tb(1)–N(2) = 2.717(6) Å. There are three different "5-FUA" ligands coordinated to terbium(III) as bidentate chelating (κ^2–), bidentate bridging ($\mu - \kappa^1$: κ^1–) as well as bridging monodentate: bidentate: monodentate ($\mu - \kappa^1 : \kappa^2 : \kappa^1$–), as shown in scheme 1(a), (b), and (c), respectively. In one type of "5-FUA" ligand, the carboxylate group coordinates to a terbium(III) ion as bidentate chelating (scheme 1a). The carboxylate group of a second type of "5-FUA" ligand coordinates to two terbium(III) ions as bidentate bridging (totally bidentate) where two oxygen atoms of the carboxylate group bridges the two adjacent terbium(III) ions, yielding an



Scheme 1. Three different coordination modes of the 5-FUA ligand.

eight-membered $\{Tb–O–C–O\}_2$ metallacycle with a –OAc group, a very interesting coordination mode of the carboxylate group (see figure 2 and scheme 1b). Another type of "5-FUA" anion acts as a tetradentate ligand, connecting three Tb^{3+} ions. The carboxylate group in this type of "5-FUA" ligand acts as both bidentate chelating and bridging group where two oxygen atoms of the carboxylate group coordinate to a terbium(III) ion, also one of these oxygen atoms bridges to another terbium atom (totally tridentate). One of carbonyl groups in this type of "5-FUA" ligand coordinates to another terbium atom (scheme 1c) acting as a bridging group from the carboxylate and carbonyl groups, forming a two-dimensional coordination polymer (figure 2).

The coordination polymers contain two parts, "node and spacer" and using common metal moieties and linking them with linear "spacer" ligands can generate the architectures. In most of these compounds, the "nodes" are formed by metal ions. Formation of coordination polymers with bridging nodes, giving coordination polymers involving polynuclear metallacycles as nodes have only recently been reported. Formation of a Tb(III) complex with "5-FUA" spacer anions provides a new class of two-dimensional coordination polymer involving carboxylate-bridged binuclear metallacycle terbium(III) complexes as nodes.

The "5-FUA" anions and uncoordinated water molecules are linked by hydrogen bonds (figure 3). The hydrogen atom (N–H) of "5-FUAA" and uncoordinated water are involved in hydrogen bonding, acting as hydrogen-bond donors with F and O atoms from "5-FUA" anions. The hydrogen bond distances d(D–H), d(H···A), d(D···A), and angle ∠(DHA)} are given in the table 3.

Supplementary material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at the Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 288413 for $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$.

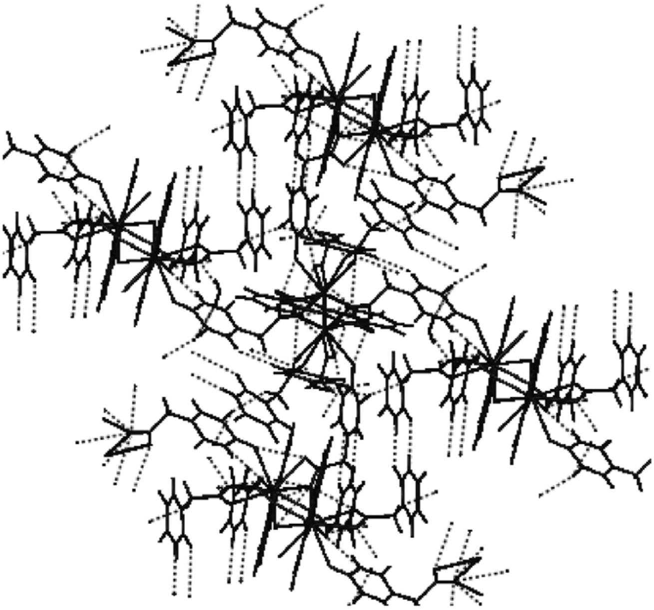


Figure 3. Hydrogen bonding in the crystal packing of $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$.

Table 3. Hydrogen bonds [Å and °] for $[Tb(phen)(5\text{-}FUA)_3]_n \cdot H_2O$.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(13)–H(13D)···F(1) [$-x+2$, $y+1/2$, $-z+3/2$]	0.85	2.59	3.201(9)	129.7
O(13)–H(13D)···F(3)	0.85	2.52	3.352(8)	164.6
O(13)–H(13C)···O(6)	0.85	1.97	2.797(8)	163.1
N(8)–H(8A)···O(2) [$-x+1$, $-y+1$, $-z+1$]	0.86	1.93	2.752(7)	159.3
N(6)–H(6A)···O(7) [$-x+1$, $-y+1$, $-z+2$]	0.86	1.94	2.787(8)	168.7
N(4)–H(4)···O(4) [$-x+1$, $-y+1$, $-z+2$]	0.86	2.01	2.869(8)	174.3

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