Mixed crystal of bis(ammonium/oxonium) tetra-aqua-μ₃-fluorido-dodecakis(μ₂-trifluoroacetato)octahedro-hexaytterbiate(III) tetrahydrate, 
[(NH₄)₁₋ₓ(H₃O)ₓ]₂[Yb₆F₈(O₂CCF₃)₁₂(H₂O)₄]·4H₂O (x = 1/4), containing a hexanuclear ytterbium(III) carboxylate complex with face-capping fluoride ligands and comprising an unusual kind of substitutional disorder

Florian Morsbach and Walter Frank*

Institut für Anorganische Chemie und Strukturchemie, Lehrstuhl II: Material-, und Strukturforschung, Heinrich-Heine-Universität Düsseldorf, D-40225, Düsseldorf, Germany. *Correspondence e-mail: wfrank@hhu.de

The reaction of ytterbium metal with ammonium trifluoroacetate in liquid ammonia resulted in a green substance comprising a substantial amount of ytterbium(II) trifluoroacetate that is a useful precursor for the oxidative synthesis of the new ytterbium(III) compound, [(NH₄)₁₋ₓ(H₃O)ₓ]₂[Yb₆F₈(O₂CCF₃)₁₂(H₂O)₄]·4H₂O (x = 1/4), in aqueous trifluoroacetic acid. This mixed ammonium/oxonium crystalline solid is the first example of a substance containing an octahedro-hexanuclear ytterbium(III) complex with μ₃-face-capping fluoride ligands. The main structural features of its [Yb₆F₈] core are non-bonding Yb···Yb distances and Yb—F bond lengths of 3.7576 (3)–3.9413 (5) and 2.2375 (17)–2.3509 (17) Å, respectively. Yb—O bond lengths involving the O atoms of $O_2O$-bridging carboxylato ligands and vertex-substituting aqua ligands are in the ranges 2.23 (4)–2.329 (2) and 2.448 (2)–2.544 (3) Å, respectively. These bond lengths are in accordance with expectations, taking into account lanthanoid contraction. Interestingly, there is a significant ammonium versus oxonium ion site dependence, not only of the hydrate water molecule positions within the solid’s hydrogen-bonding framework, but also of the coordination sites of one carboxylato and one aqua ligand in the hexanuclear complex.

1. Chemical context

The stabilizing influence of liquid ammonia as a reaction medium on $Ln^{II}$ of certain lanthanoids ($Ln$) is well known (Warf & Korst, 1956; Warf, 1970). Selected ytterbium(II) compounds such as bis(cyclopentadienyl)ytterbium(II) (Fischer & Fischer, 1965; Hayes & Thomas, 1969), ytterbium(II) phosphide (Pytlewsky & Howell, 1969), ytterbium(II) amide (Hadenfeldt & Juza, 1969; Hadenfeldt et al., 2016) and ytterbium(II) halides (Howell & Pytlewski, 1969) can be obtained by precipitation reactions in liquid ammonia. Adapting this procedure in explorative attempts to synthesize ytterbium(II) trifluoroacetate, we obtained a green mixture of substances, the color of which indicating the presence of Yb$^{II}$ ions. By dissolution experiments in trifluoroacetic acid and subsequent crystallization under non-inert conditions, we obtained colorless crystals of
the title compound. The formation of this substance requires not only redox reactions with the change of the oxidation state from 0 to +II and from +II to +III, but also an activation of the C—F bonds of the trifluoroacetate anion (Rillings & Roberts, 1974). This is evident not only from the presence of fluoroido ligands as part of the octahedro-hexanuclear complex anion of the title compound, \([\text{[NH}_4]_{1-x} \text{(H}_3\text{O})_x \text{]}_2 \text{[Yb}_6\text{F}_8\text{(O}_2\text{CCF}_3)_{12-} \text{(H}_2\text{O})_4]\) 4\text{H}_2\text{O} (x = 0.25), but also from the presence of ammonium fluoride in the greenish precipitate from the reaction of ytterbium metal with ammonium trifluoroacetate in liquid ammonia.

2. Structural commentary

In the course of the crystal-structure refinement, the crystal under investigation turned out to be a mixed crystal characterized by \(\text{NH}_4^+/\text{H}_3\text{O}^+\) substitution. However, the structure model with disorder of the cation sites is much more complicated because the disorder not only affects the latter, but also other parts of the crystal structure. Fig. 1 shows the asymmetric unit of the title compound, separated in terms of the \(\text{NH}_4^+\)-containing partial occupation site (part a) and in terms of the \(\text{H}_3\text{O}^+\)-containing partial occupation site (part b). Both partial occupation site units comprise three \(\text{Yb}^{\text{III}}\) ions, four fluoride anions, six trifluoroacetate anions and two water molecules, all in general position and establishing one half of a centrosymmetric octahedro-hexanuclear \([\text{Yb}_6\text{F}_8\text{(O}_2\text{CCF}_3)_{12-} \text{(H}_2\text{O})_4]\) \(2^-\) complex. Also in general positions, one \(\text{NH}_4^+\) or \(\text{H}_3\text{O}^+\) cation and two water molecules complete the asymmetric unit. The charge balance of the double-negatively charged complex ion is ensured by two symmetry-related cations. The most prominent moiety in both cases is the octahedro-hexanuclear anionic complex, formed by six \(\text{Yb}^{\text{III}}\) ions with non-bonding \(\text{Yb} \cdot \cdot \cdot \text{Yb}\) distances of 3.7576 (3)–3.9413 (5) Å (mean 3.83 Å, see Table 1), the eight octahedral faces of which are capped by \(\mu_3\)-fluorido ligands. In the \(\text{NH}_4^+\) case, all twelve octahedral edges of the central \([\text{Yb}_6\text{F}_8]\) core are bridged by \(\mu_2\)-trifluoroacetato ligands. \(\text{Yb}^1\) is eightfold coordinated with a typical square-antiprismatic coordination polyhedron (Karraker, 1970). Water molecules additionally coordinate the octahedral vertices of the \(\text{Yb}^2\) and \(\text{Yb}^3\) sites and complete the coordination sphere of these \(\text{Yb}^{\text{III}}\) ions, giving a ninefold coordination that results in mononcapped square-antiprismatic coordination polyhedra (Fig. 2a).

![Figure 1](image-url)

Asymmetric unit of \([\text{[NH}_4]_{1-x} \text{(H}_3\text{O})_x \text{]}_2 \text{[Yb}_6\text{F}_8\text{(O}_2\text{CCF}_3)_{12-} \text{(H}_2\text{O})_4]\) 4\text{H}_2\text{O} (x = 1/4), as related to the \(\text{NH}_4^+\)-containing partial occupation site (a) and as related to the \(\text{H}_3\text{O}^+\)-containing partial occupation site (b), shown separately with the same view direction and the same scaling. Displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms are drawn with an arbitrary radius. The \(\text{CF}_3\) groups at \(\text{C}_5\) and \(\text{C}_{11}\) suffer from rotational disorder that is not related to the cation substitution; only \(\text{F}\) atoms of the major occupied sites are shown. The directions of further \(\text{Yb} \cdot \cdot \cdot \text{O}\) and \(\text{Yb} \cdot \cdot \cdot \text{F}\) bonds are given by truncated sticks, the directions of hydrogen-bonding by segmented blue sticks. Note the coincidence of most parts of the partial occupation site models and the significant differences in the cation/water region and the coordination spheres of \(\text{Yb}^2\) and \(\text{Yb}^3\).
In the H$_3$O$^+$ case, one trifluoroacetato ligand binds to Yb$_2$ monodentately only, while two water molecules coordinate to Yb$_3$ in return (Fig. 1), giving an eightfold coordination of Yb$_1$ and Yb$_2$ and a ninefold coordination for Yb$_3$ (Fig. 2). At first view, the nature of the cation seems to influence the remaining parts of the structure and even to some extent the ligand substitution pattern of the hexanuclear complex. However, we cannot exclude the possibility that the presence of the two isomeric anions (related to hydration) is the origin of the cation substitution. The Yb—O bond lengths of 2.23 (4)–2.32 (4) Å (mean 2.30 Å), and the O—C—O bond angles of 129.6 (3)–132.2 (3)$^\circ$ (mean 129.9$^\circ$) of the trifluoroacetato ligands are in typical ranges for the bidentately bridging coordination mode of carboxylate ligands (Rohde & O'Keeffe, 1991). Relevant Yb—F and Yb—O bond lengths are given in Table 1, along with the corresponding empirical bond valences, $s_i$. The Yb—F bond lengths and the bond-valence sums $S$ of 3.01–3.13 valence units give striking structural evidence for the presence of fluorido ligands. Comparisons of the complex anion with the one in the very recent crystal-structure determination of an octahedro-hexanuclear terbium(III) complex containing a [Tb$_6$F$_8$] core (Ling et al., 2020) and with some europium(III) complexes containing [Eu$_6$F$_8$] cores (Morsbach et al., 2022) reveal that the non-bonding Ln...Ln distances [mean 3.97 Å ($Ln$ = Tb) and 4.00 Å ($Ln$ = Eu)] as well as the Ln—F (mean 2.38 and 2.38 Å) and Ln—O bond lengths (mean 2.34 and 2.40 Å) in complexes of this type are influenced by the lanthanoid contraction, with these structural parameters decreasing from Eu to Yb due to the smaller ionic radius of Yb$^{III}$ compared to Tb$^{III}$ and Eu$^{III}$: 1.04 Å vs. 1.10 Å and 1.12 Å (all values for CN 9; Shannon, 1976).

Table 1
Selected structural parameters (Å) and empirical bond valences $s_i$ (valence units) for Yb$_1$–Yb$_3$.

| $X$   | $Y$   | $d_i$   | s.o.f. of atom $Y$ | $s_i$ |
|-------|-------|---------|-------------------|-------|
| Yb$_1$—F1 | 2.2375 (17) | 1 | 0.38 |
| Yb$_1$—F2 | 2.2382 (17) | 1 | 0.37 |
| Yb$_1$—F3 | 2.2431 (17) | 1 | 0.37 |
| Yb$_1$—F4 | 2.2444 (17) | 1 | 0.37 |

Symmetry code: (vi) $x-x+1, y+y+1, z-z+1$.

In the H$_2$O$^+$ case, one trifluoroacetato ligand binds to Yb$_2$ monodentately only, while two water molecules coordinate to Yb$_3$ in return (Fig. 1), giving an eightfold coordination of Yb$_1$ and Yb$_2$ and a ninefold coordination for Yb$_3$ (Fig. 2b). At first view, the nature of the cation seems to influence the remaining parts of the structure and even to some extent the ligand substitution pattern of the hexanuclear complex. However, we cannot exclude the possibility that the presence of the two isomeric anions (related to hydration) is the origin of the cation substitution. The Yb—O bond lengths of 2.23 (4)–2.32 (2) Å (mean 2.30 Å), and the O—C—O bond angles of 129.6 (3)–132.2 (3)$^\circ$ (mean 129.9$^\circ$) of the trifluoroacetato ligands are in typical ranges for the bidentately bridging coordination mode of carboxylate ligands (Rohde & O'Keeffe, 1991). Relevant Yb—F and Yb—O bond lengths are given in Table 1, along with the corresponding empirical bond valences for each bond, $s_i$. The Yb—F bond lengths and the bond-valence sums $S$ of 3.01–3.13 valence units give striking structural evidence for the presence of fluorido ligands. Comparisons of the complex anion with the one in the very recent crystal-structure determination of an octahedro-hexanuclear terbium(III) complex containing a [Tb$_6$F$_8$] core (Ling et al., 2020) and with some europium(III) complexes containing [Eu$_6$F$_8$] cores (Morsbach et al., 2022) reveal that the non-bonding Ln...Ln distances [mean 3.97 Å ($Ln$ = Tb) and 4.00 Å ($Ln$ = Eu)] as well as the Ln—F (mean 2.38 and 2.38 Å) and Ln—O bond lengths (mean 2.34 and 2.40 Å) in complexes of this type are influenced by the lanthanoid contraction, with these structural parameters decreasing from Eu to Yb due to the smaller ionic radius of Yb$^{III}$ compared to Tb$^{III}$ and Eu$^{III}$: 1.04 Å vs. 1.10 Å and 1.12 Å (all values for CN 9; Shannon, 1976).
three anions establishing a tetrahedral pocket than to the other three.

Thus, each cation is significantly closer to one of the [010] or in the reverse direction and to a lesser extent along [010] or in the reverse direction. This offset is along a similar fashion. With respect to the primitive unit cell, this offset is along [101] or in the reverse direction and to a lesser extent along [101] or in the reverse direction. Thus, each cation is significantly closer to one of the four anions establishing a tetrahedral hole than to the other three.

![Schematic packing diagram. The bulky fluoridocarboxylate anions are represented by octahedra, the cation positions are given by dot-centered squares. The distorted fcc packing of these voluminous anions can be recognized. As shown in Fig. 3 in more detail, in a strongly off-center mode the small cations occupy all tetrahedral interstices of this packing. The hexanuclear ytterbiate(III) anions as well as all other moieties are engaged in an extended hydrogen-bonded supramolecular network (Table 2). All hydrogen bonds have medium to weak strengths. A remarkable segment of this network is established by two symmetry-related pairs of water molecules around a center of inversion.](image)

### Table 2

| D—H ·· ·A | D—H | H ·· ·A | D ·· ·A | D—H ·· ·A |
|-----------|-----|--------|--------|--------|
| N1—H12···O6 | 0.91 | 2.21  | 2.883 (8) | 131 |
| N1—H15···O17<sup>a</sup> | 0.91 | 1.86  | 2.766 (7) | 172 |
| N1—H13···O10 | 0.91 | 2.08  | 2.853 (10) | 142 |
| N1—H14···O2 | 0.91 | 1.95  | 2.837 (9) | 165 |
| O1—H2···O2A | 0.84 | 1.78  | 2.619 (18) | 175 |
| O1—H3···O9A<sup>a</sup> | 0.84 | 2.01  | 2.842 (16) | 173 |
| O1—H4···O10 | 0.84 | 2.30  | 3.03 (3) | 145 |
| O2—H4···O3 | 0.83 (1) | 1.91 (3) | 2.704 (11) | 159 (7) |
| O2—H5···O12 | 0.83 (1) | 2.31 (5) | 2.978 (7) | 138 (6) |
| O3—H6···O2<sup>b</sup> | 0.85 (2) | 2.22 (2) | 3.055 (10) | 167 (8) |
| O3—H7···O17<sup<c>iii</sup> | 0.85 (2) | 2.01 (2) | 2.835 (9) | 163 (8) |
| O2A—H4A···F19A | 0.83 (1) | 1.90 (7) | 2.68 (2) | 156 (17) |
| O2A—H5A···O3A<sup>a</sup> | 0.83 (1) | 2.35 (14) | 2.96 (3) | 131 (16) |
| O3A—H7A···O2A | 0.84 (2) | 2.20 (15) | 2.91 (4) | 143 (25) |
| O3A—H6A···O9A<sup>iv</sup> | 0.83 (2) | 2.6 (2) | 3.03 (4) | 115 (19) |
| O16—H8···O9 | 0.83 (2) | 2.28 (6) | 2.639 (10) | 107 (4) |
| O16—H8A···O16<sup>c</sup> | 0.84 (2) | 2.07 (2) | 2.903 (5) | 179 (17) |
| O16—H9···F16<sup>c</sup> | 0.82 (2) | 2.17 (2) | 2.954 (3) | 160 (4) |
| O17—H10···O8 | 0.84 (2) | 2.25 (8) | 2.593 (7) | 105 (7) |
| O17—H10···O13<sup>c</sup> | 0.81 (2) | 2.22 (5) | 2.754 (4) | 123 (5) |
| O17A—H10A···O16 | 0.83 (1) | 1.92 (2) | 2.56 (3) | 134 (5) |

Symmetry codes: (i) x, y+1, z; (ii) −x, −y−1, −z+1; (iii) x+1, y, −z+1; (iv) x, −y+1, z; (v) x+1, z; (vi) −x+1, −y+1, −z+1.

### 3. Supramolecular features

Approximating the hexanuclear anionic complex as a bulky sphere, a distorted fcc packing of these voluminous anions can be recognized. As shown in Fig. 3 in more detail, in a strongly...
Depending on the nature of the cation, the positions and orientations of these water molecules are significantly different, as shown in Fig. 4. Note, that the partial occupation sites occupied by O2 and O3 are related to NH4+ and those occupied by O2A and O3A are related to H3O+. In both cases, the graph set descriptor \( R_2^2(8) \) can be assigned to the hydrogen-bond motif (Etter et al., 1990). However, a different orientation of the hydrogen-bond-donor direction is given within the ring-shaped system. In the NH4+ case, with the exception of four H atoms at the vertices (H5, H7, H5″ and H7″), the \((H_2O)_4\) unit is almost planar (Fig. 4a), while in the H3O+ case, all H atoms are out-of-plane with the O atoms (Fig. 4b). In both cases, two further four-membered ring motifs are annealed to the \((H_2O)_4\) unit, assigned to the graph-set descriptor \( R_2^2(8) \). In these motifs, two water molecules, a cation and, in the case of NH4+ occupying the cation position, an aqua ligand (including O17) from the \( [Yb_6F_8(O_2CCF_3)_{12}(H_2O)_4]^2^- \) complex anion are involved. In the case of H3O+ occupying the cation position, O9A from the monodentately bonding trifluoroacetate ligand at Yb2 takes the role of O17 as a double acceptor. With further O—H···O, O—H···F, and N—H···O hydrogen bonds, the entire tricyclic hydrogen-bonding motif connects in total four of the hexanuclear complexes, each of which gives further connections in three symmetry-related directions. As expected, due to the higher solvation energy free of H2O+ compared to NH4+ (Taft et al., 1978; Saielli, 2010), the primary hydrogen-bonding interaction of H2O+ is significantly stronger than that of NH4+: \( |O1···O2A| = 2.619 (18) \AA \) vs. \( |N1···O17| = 2.766 (7) \AA \).

4. Database survey
A search of the Cambridge Structural Database (CSD; version 5.43, update of November 2021; Groom et al., 2016) resulted in 80 hits for isolated octahedro-hexanuclear lanthanoid complexes with eight \( \mu_2 \)-face-capping ligands of any type, excluding a \( \mu_6 \)-central atom. Only two of these contain eight \( \mu_5 \)-halogenido ligands of any type, including the carboxylato fluoro complex with a \([Tb_6F_8] \) core (KUWMOH, Ling et al., 2020) and a cyclopentadienyl iodo complex with a \([Yb_6I_8] \) core (TUFWEW, Constantine et al., 1996). Six of the 80 complexes are ytterbium complexes, viz. the aforementioned iodo complex, three octa-\( \mu_2 \)-hydroxido complexes (MINVAI, da Cunha et al., 2013; HELNAQ, Zhang et al., 2018; XUKCAK, Luo et al., 2020) and one tetra-\( \mu_2 \)-oxidotetra-\( \mu_2 \)-hydroxido complex (YINFEJ, Feng et al., 2019). The first, the second and the fourth of these are parts of metal-organic frameworks (MOFs). Furthermore, there is a hexa-\( \mu_3 \)-oxidodi-\( \mu_2 \)-hydroxido complex (KIFVAZ, Duan et al., 2018). A search in the ICSD (version 2021.2; Belsky et al., 2002) for structures containing both NH4+ and H2O+ ions, resulted in ten hits. Seven of these show NH4+/H2O+ substitutional disorder. Three of the seven disordered structures are mixed ammoniojarosite–hydroniumjarosite phases, \((NH_4)_x(H_2O)_{4-x}F_e_2(SO_4)_3(OH)_6 \) (#16020–16022, Basciano & Peterson, 2007). Furthermore, there are two phosphates (#73847–73848, Ferey et al., 1993), a molybdatophosphate (#212, Boeyens et al., 1976) and an oxide (#37066, Thomas & Farrington, 1983). However, for none of these structures cation-dependent further partial occupation sites are reported.

5. Synthesis and crystallization
All chemicals were obtained from commercial sources and used as purchased. In a representative experiment, 0.584 g (0.337 mmol) of ytterbium were dissolved in approximately 50 ml of liquid ammonia (dried over sodium) to which 0.903 g (0.675 mmol) of ammonium trifluoroacetate were added. The ammonia was evaporated, and the residue was dried in \textit{vacuo} until a pressure of 10^{-3} hPa was reached. 0.816 g of a greenish powder were obtained. 100 mg of this powder were stirred in 2 ml of anhydrous trifluoroacetic acid, and the insoluble portions were allowed to settle overnight. The supernatant solution was transferred into an ampoule and stored open in air. Colorless crystals of the title compound grew within one week. A suitable single crystal for X-ray crystal structure determination was selected directly from the mother liquor. An IR spectrum was recorded with a \textit{Spectrum Two FT–IR} spectrometer (Perkin Elmer Inc., 2008), equipped with a LiTaO3 detector (4000–350 cm^{-1}) and an ATR unit. Band assignments were made according to metal trifluoroacetate salts (Baillie et al., 1968; Faniran & Patel, 1976): \( v(O–H): 3374, 3287 \) (w); \( v_2(COO): 1665 \) (s); \( 1613 \) (m); \( 1569 \) (m); \( v_4(COO): 1473 \) (m); \( 1342 \) (w); \( v(C–F): 1204, 1142 \) (s); \( v(C–C): 849 \) (m); \( \delta(CF_2): 794 \) (m); \( \delta(O–C–O): 724 \) (s); \( 687 \) (w); \( \delta(CO): 613, 522, 452 \) (vw). A CHN analysis was performed with a \textit{vario MICRO cube} (Elementar Analysensysteme GmbH, 2015). Analysis calculated for \( C_{24}H_{23.50}N_{1.50}O_{32.50}F_{44}Yb_6 \) (2727.15 g mol^{-1}): C 10.57, H 0.87, N 1.0; found: C 10.7, H 0.8, N 1.0.

6. Refinement
Crystal data along with data collection and structure refinement details are summarized in Table 3. After having completed the primary structural model, (a) physically non-meaningful anisotropic displacement parameters, (b) features appearing in the difference-electron density map in the course of further refinement cycles and (c) analysis of potential hydrogen-bonding orientations clearly indicated disorder that refers to: (i) position and nature of the cation (NH4+ vs. H2O+); (ii) position and coordination mode of the complete carboxylato ligand with atoms O8 and O9, (iii) position (coordination site) of the aqua ligand with O17, (iv) orientation of the aqua ligand with O16, (v) rotational orientation of four of the six CF3 groups and (vi) position and orientation of the two hydrate water molecules. The refinement of site-occupation factors finally proved the disorder according to (i), (ii), (iii), (iv), (vi) and the rotational orientations of three of the four CF3 groups addressed in (v) to be directly dependent. In the final stages of a converging refinement, for these dependent sites a common occupation factor was introduced and refined to 0.749 (4) for NH4+ and its related partial occupation site moieties, giving 0.251 (4) for H2O+ and its...
related moieties. When involved in disorder, NH₄⁺ and H₂O⁺ ions can hardly be distinguished in a structure refinement based on X-ray diffraction data alone. All substances related to the class of the title compound showed somewhat too high proportions for N in the combustion analysis, and due to the complex vibration spectra, an identification of O—H or N—H stretching modes in the IR spectrum is not possible. In complex vibration spectra, an identification of O—H or N—H bond lengths could hardly be distinguished in a structure refinement. When involved in disorder, NH₄⁺ ions can hardly be distinguished in a structure refinement.

The much shorter O···O distance of 2.619 (18) Å from the lower-occupied site to the O atom of the next water molecule is typical for comparatively strong O···O hydrogen bonds, but out of the limits of expectation for N···O···O bonds to water molecules [Meot-Ner (Mautner), 2005]. Finally, if the lower-occupied site were assumed to be a NH₄⁺ ion, no suitable hydrogen-bond acceptor could be identified for an additional, fourth hydrogen bond. All disordered parts of the structure were subjected to appropriate bond lengths and angles and anisotropic displacement restraints or constraints. The C—F bond lengths of the disordered CF₃ groups related to C4, C10, C12, (C6) were restrained to 1.32 Å within a s. u. of 0.02 Å (0.002 Å), combined with default F—C same distance and with strongly restrictive isotropic displacement restraints for all F atoms. No restraints were needed for the two CF₃ groups not suffering from disorder. For the CF₃ group related to C6, which suffers from both positional dependent and independent rotational disorder, more restrictive C—F bond lengths restraints (see above) had to be used and the C—C bond length was restrained to 1.52 Å within a s. u. of 0.02 Å. For atoms at partial occupation sites in close proximity, in an approximative manner equivalent anisotropic displacement constraints have been applied, namely for the pairs N1/O1, O2/O2, O3/O3, O8/O8A, O9/O17A, C12/C12A. The NH₄⁺ ion was treated in the refinement as a rigid group with idealized tetrahedral shape and N—H bond lengths constrained to 0.91 Å. The H₂O⁺ cation was included as a rigid flat pyramid with O···H bond lengths constrained to 0.84 Å and the pyramidalization defined by H···H distances constrained to 1.39 Å. The hydrate water molecules related to O2 and O2A were treated as rigid groups with O···H bond lengths of 0.83 Å and H···O···H angles adjusted to 105.4°. The O···H bond lengths of the aqua ligands including O16, O16A, O17, O17A and of the hydrate water molecules including O3 and O3A were restrained to 0.83 Å within an s.u. of 0.02 Å, the corresponding H···H distances to 1.32 Å within an s.u. of 0.04 Å defining H···O···H angles of 105 (4)–109 (4)°. U(eq)(H) values of all H atoms were set to 1.5U(eq) of the parent atoms.

Acknowledgements

Technical support by E. Hammes and T. Herrmann is gratefully acknowledged.

Funding information

Financial support of this research was provided by: Jürgen Manchot Stiftung (scholarship to Florian Morsbach).

Table 3
Experimental details.

| Crystal data | Chemical formula |
|--------------|-----------------|
| [NH₄]⁺···(H₂O)⁺[Yb₆F₆(O₂CCF₃)₁₂(H₂O)₄]4H₂O (x = 1/4) | Mₐ |
| 2727.15 | Crystal system, space group |
| Monoclinic, P2₁/n | Temperature (K) |
| 120 | No. of reflections |
| 7213 | F(Å²) |
| 3146.3 (6) | No. of parameters |
| 717 | "μ (mm⁻¹)" |
| 9.04 | Crystal size (mm) |
| 0.17 × 0.11 × 0.05 | Data collection |
| Diffractometer |
| Bruker APEX-II CCD | Absorption correction |
| Multi-scan (SADABS, Krause et al., 2015) |
| Tmin–Tmax | No. of measured, independent and observed [I > 2σ(I)] reflections |
| 0.665–1.000 | 48765, 7213, 6768 |
| Rint | (sin θ/λ)max (Å⁻¹) |
| 0.035 | 0.650 |
| Refinement | R[F² > 2σ(F²)], wR(F²), S |
| 0.019, 0.044, 1.08 | No. of reflections |
| 7213 | No. of parameters |
| 717 | No. of restraints |
| 268 | H-atom treatment |
| H atoms treated by a mixture of independent and constrained refinement |

Δρmax, Δρmin (e Å⁻³) |
| 0.96, —0.89 |

Computer programs: APEX2 and SAINT (Bruker, 2014), SHELXTL (Sheldrick, 2015), DIAMOND (Brandenburg, 2020), SHELXL (Sheldrick, 2008) and pubICIF (Westrip, 2010).
Mixed crystal of bis(ammonium/oxonium) tetraaquatoctahedral-fluorido-dodekafluoroacetato-octahedro-hexaytterbiate(III) tetrahydrate, [(NH₄)₁₋ₓ(H₃O)ₓ]₂[Yb₆F₈(O₂CCF₃)₁₂(H₂O)₄]·₄H₂O (x = 1/4), containing a hexanuclear ytterbium(III) carboxylate complex with face-capping fluoride ligands and comprising an unusual kind of substitutional disorder

Florian Morsbach and Walter Frank

Computing details

Data collection: APEX2 (Bruker, 2014); cell refinement: SAINT (Bruker, 2014); data reduction: SAINT (Bruker, 2014); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: DIAMOND (Brandenburg, 2020), SHELXTL (Sheldrick, 2008); software used to prepare material for publication: publCIF (Westrip, 2010).

Bis(ammonium/oxonium) tetraaquatoctahedral-fluorido-dodekafluoroacetato-octahedro-hexaytterbiate(III) tetrahydrate

Crystal data

(NH₄)₁₋ₓ(H₃O)ₓ[Yb₆(F₃CF₂O)₁₂F₈(H₂O)₄]·₄H₂O

F(000) = 2508

Dₐ = 2.879 Mg m⁻³

Mo Ka radiation, λ = 0.71073 Å

Cell parameters from 9176 reflections

θ = 2.3–30.6°

µ = 9.04 mm⁻¹

T = 120 K

Block, colorless

0.17 × 0.11 × 0.05 mm

Data collection

Bruker APEXII CCD

diffraectrometer

Radiation source: sealed tube

θ and ω scans

Absorption correction: multi-scan

(SADABS; Krause et al., 2015)

T(υ) = 0.665, T(max) = 1.000

48765 measured reflections

7213 independent reflections

6768 reflections with I > 2σ(I)

R(sin) = 0.035

θ(max) = 27.5°, θ(min) = 1.8°

h = -15→15

k = -22→22

l = -19→19
Refinement

Refinement on $F^2$
Least-squares matrix: full
$R[F^2] = 0.019$
$\omega R(F^2) = 0.044$
$S = 1.08$
7213 reflections
717 parameters
268 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement

$\omega = 1/[\sigma^2(F_o^2) + (0.0153P)^2 + 6.7213P]$
$\Delta \rho_{\text{max}} = 0.96 \text{ e Å}^{-3}$
$\Delta \rho_{\text{min}} = -0.89 \text{ e Å}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)

|     | x         | y         | z         | U_{iso}*/U_{eq} | Occ. (<1) |
|-----|-----------|-----------|-----------|-----------------|-----------|
| Yb1 | 0.45797 (2) | 0.64420 (2) | 0.47775 (2) | 0.01292 (4)     | 0.01292 (4) |
| Yb2 | 0.41912 (2) | 0.47533 (2) | 0.31832 (2) | 0.01477 (4)     | 0.01477 (4) |
| Yb3 | 0.71762 (2) | 0.52450 (2) | 0.47250 (2) | 0.01400 (4)     | 0.01400 (4) |
| F1  | 0.54171 (14)| 0.56846 (10)| 0.39369 (11)| 0.0148 (3)      | 0.0148 (3)  |
| F2  | 0.61494 (14)| 0.59078 (9) | 0.56047 (12)| 0.0150 (3)      | 0.0150 (3)  |
| F3  | 0.34576 (14)| 0.54633 (10)| 0.41953 (11)| 0.0144 (3)      | 0.0144 (3)  |
| F4  | 0.58154 (14)| 0.43124 (9) | 0.41390 (11)| 0.0145 (3)      | 0.0145 (3)  |
| F5  | 0.7250 (3)  | 0.77519 (17)| 0.30917 (17)| 0.0626 (9)      | 0.0626 (9)  |
| F6  | 0.85133 (18)| 0.78640 (15)| 0.43135 (19)| 0.0484 (7)      | 0.0484 (7)  |
| F7  | 0.6979 (2)  | 0.84737 (12)| 0.4135 (2)  | 0.0457 (6)      | 0.0457 (6)  |
| F8  | 0.4230 (4)  | 0.7285 (3) | 0.1531 (4) | 0.0512 (14)     | 0.749 (4)   |
| F9  | 0.2777 (4)  | 0.7738 (3) | 0.1940 (5) | 0.0304 (11)     | 0.749 (4)   |
| F10 | 0.2603 (5)  | 0.6762 (4) | 0.1066 (4) | 0.0437 (14)     | 0.749 (4)   |
| F11 | 0.3133 (12)| 0.6858 (12)| 0.1283 (11)| 0.048 (5)       | 0.048 (5)   |
| F12 | 0.4019 (14)| 0.7031 (10)| 0.1268 (11)| 0.056 (5)       | 0.056 (5)   |
| F13 | 0.3186 (15)| 0.7817 (9) | 0.1959 (18)| 0.053 (6)       | 0.053 (6)   |
| F14 | 0.7963 (4)  | 0.5569 (5) | 0.1769 (4) | 0.079 (2)       | 0.079 (2)   |
| F15 | 0.5733 (9)  | 0.4814 (4) | 0.1043 (6) | 0.077 (3)       | 0.077 (3)   |
| F16 | 0.6286 (6)  | 0.5964 (4) | 0.1241 (5) | 0.069 (2)       | 0.069 (2)   |
| O8  | 0.5527 (8)  | 0.4900 (7) | 0.2337 (7) | 0.0203 (13)     | 0.749 (4)   |
| O9  | 0.7214 (8)  | 0.5232 (4) | 0.3210 (7) | 0.0178 (12)     | 0.749 (4)   |
| C5  | 0.6511 (4)  | 0.5141 (2) | 0.2478 (3) | 0.0176 (9)      | 0.0176 (9)  |
| C6  | 0.6887 (3)  | 0.5381 (2) | 0.1630 (3) | 0.0293 (12)     | 0.0293 (12) |
| F11A| 0.5725 (10)| 0.4478 (6) | 0.0149 (6) | 0.051 (3)       | 0.051 (3)   |
| F12A| 0.5402 (13)| 0.5632 (6) | 0.0381 (10)| 0.081 (5)       | 0.081 (5)   |
| F13A| 0.6809 (12)| 0.5075 (12)| 0.1199 (14)| 0.082 (6)       | 0.082 (6)   |
| O8A | 0.532 (3)   | 0.482 (2)  | 0.222 (3)  | 0.0203 (13)     | 0.0203 (13) |
| O9A | 0.3984 (10)| 0.4521 (6) | 0.1033 (8) | 0.031 (3)       | 0.031 (3)   |
| Atom | U1   | U2   | U3   | U4   | U5   |
|------|------|------|------|------|------|
| C5A  | 0.4914 (10) | 0.4755 (7) | 0.1383 (8) | 0.017 (3) | 0.251 (4) |
| C6A  | 0.5735 (11) | 0.4983 (5) | 0.0796 (6) | 0.036 (4) | 0.251 (4) |
| C6B  | 0.6887 (3) | 0.5381 (2) | 0.1630 (3) | 0.0293 (12) | 0.2247 (11) |
| F11B | 0.6105 (11) | 0.5475 (10) | 0.0931 (9) | 0.059 (4) | 0.2247 (11) |
| F12B | 0.7644 (11) | 0.4909 (7) | 0.1435 (8) | 0.046 (3) | 0.2247 (11) |
| F13B | 0.7478 (12) | 0.6044 (7) | 0.1744 (8) | 0.047 (3) | 0.2247 (11) |
| F14  | 0.1535 (2) | 0.7283 (17) | 0.63021 (17) | 0.0524 (7) | 0.2247 (11) |
| F15  | 0.1150 (2) | 0.7817 (12) | 0.50072 (18) | 0.0403 (6) | 0.2247 (11) |
| F16  | 0.01836 (18) | 0.68636 (13) | 0.52708 (19) | 0.0430 (6) | 0.2247 (11) |
| F17  | 0.4294 (4) | 0.8118 (3) | 0.7341 (4) | 0.058 (2) | 0.608 (11) |
| F18  | 0.5947 (6) | 0.8386 (3) | 0.7221 (4) | 0.053 (2) | 0.608 (11) |
| F19  | 0.5704 (8) | 0.7692 (3) | 0.8300 (3) | 0.065 (3) | 0.608 (11) |
| F17A | 0.6285 (6) | 0.7902 (5) | 0.8017 (6) | 0.045 (3) | 0.392 (11) |
| F18A | 0.4547 (8) | 0.7724 (5) | 0.7927 (7) | 0.060 (3) | 0.392 (11) |
| C12  | 0.9654 (5) | 0.5666 (4) | 0.7508 (4) | 0.0251 (11) | 0.749 (4) |
| F20  | 0.9848 (3) | 0.5158 (3) | 0.8172 (3) | 0.0571 (12) | 0.749 (4) |
| F21  | 1.0494 (4) | 0.5633 (3) | 0.7093 (3) | 0.0490 (14) | 0.749 (4) |
| F22  | 0.9698 (3) | 0.6338 (2) | 0.7904 (3) | 0.0528 (12) | 0.749 (4) |
| C12A | 0.9711 (13) | 0.5553 (11) | 0.7414 (13) | 0.0251 (11) | 0.251 (4) |
| F20A | 1.0361 (15) | 0.5984 (8) | 0.7057 (12) | 0.054 (5) | 0.251 (4) |
| F21A | 0.9744 (10) | 0.5820 (11) | 0.8220 (8) | 0.066 (4) | 0.251 (4) |
| F22A | 1.0184 (9) | 0.4883 (6) | 0.7513 (10) | 0.061 (4) | 0.251 (4) |
| N1   | 0.2926 (7) | 0.8306 (4) | 0.3919 (6) | 0.0273 (12) | 0.749 (4) |
| H12  | 0.301083 | 0.802939 | 0.343121 | 0.041* | 0.749 (4) |
| H13  | 0.265981 | 0.799714 | 0.430668 | 0.041* | 0.749 (4) |
| H14  | 0.360537 | 0.850338 | 0.420455 | 0.041* | 0.749 (4) |
| H15  | 0.242715 | 0.869256 | 0.373385 | 0.041* | 0.749 (4) |
| O1   | 0.2814 (19) | 0.8472 (13) | 0.4011 (18) | 0.0273 (12) | 0.251 (4) |
| H1   | 0.264846 | 0.800676 | 0.402434 | 0.041* | 0.251 (4) |
| H2   | 0.337858 | 0.858452 | 0.442138 | 0.041* | 0.251 (4) |
| H3   | 0.225795 | 0.875305 | 0.402624 | 0.041* | 0.251 (4) |
| O2   | 0.5001 (5) | 0.8750 (4) | 0.5075 (4) | 0.0683 (19) | 0.749 (4) |
| H4   | 0.544 (5) | 0.911 (3) | 0.525 (4) | 0.102* | 0.749 (4) |
| H5   | 0.496 (7) | 0.851 (3) | 0.554 (2) | 0.102* | 0.749 (4) |
| O3   | 0.6573 (7) | 0.9867 (5) | 0.5240 (5) | 0.0665 (17) | 0.749 (4) |
| H6   | 0.616 (6) | 1.027 (3) | 0.509 (6) | 0.100* | 0.749 (4) |
| H7   | 0.711 (5) | 0.998 (4) | 0.569 (4) | 0.100* | 0.749 (4) |
| O2A  | 0.4546 (17) | 0.8903 (14) | 0.5274 (14) | 0.0683 (19) | 0.251 (4) |
| H4A  | 0.491 (13) | 0.879 (7) | 0.579 (4) | 0.102* | 0.251 (4) |
| H5A  | 0.46 (2) | 0.9376 (15) | 0.525 (9) | 0.102* | 0.251 (4) |
| O3A  | 0.668 (3) | 0.9730 (17) | 0.5589 (18) | 0.0665 (17) | 0.251 (4) |
| H6A  | 0.729 (11) | 0.956 (12) | 0.590 (16) | 0.100* | 0.251 (4) |
| H7A  | 0.628 (16) | 0.934 (8) | 0.543 (18) | 0.100* | 0.251 (4) |
| O4   | 0.74437 (19) | 0.65322 (13) | 0.44643 (16) | 0.0212 (5) | 0.251 (4) |
| O5   | 0.59075 (19) | 0.72520 (12) | 0.44714 (15) | 0.0194 (5) | 0.251 (4) |
| O6   | 0.38017 (19) | 0.69039 (13) | 0.33511 (15) | 0.0198 (5) | 0.251 (4) |
| O7   | 0.35962 (19) | 0.58759 (13) | 0.24358 (15) | 0.0203 (5) | 0.251 (4) |
|   |       |       |       |       |       |       |
|---|-------|-------|-------|-------|-------|-------|
| O10 | 0.28607 (18) | 0.69187 (12) | 0.48928 (15) | 0.0183 (4) | 0.749 (4) |
| O11 | 0.18769 (19) | 0.59112 (13) | 0.52273 (16) | 0.0214 (5) | 0.749 (4) |
| O12 | 0.49566 (19) | 0.72565 (12) | 0.60049 (15) | 0.0185 (5) | 0.749 (4) |
| O13 | 0.5663 (2) | 0.65211 (13) | 0.72162 (15) | 0.0208 (5) | 0.749 (4) |
| O14 | 0.84720 (19) | 0.54572 (14) | 0.60512 (16) | 0.0226 (5) | 0.749 (4) |
| O15 | 0.76951 (18) | 0.55146 (13) | 0.72604 (15) | 0.0204 (5) | 0.749 (4) |
| O16 | 0.9075 (2) | 0.54443 (14) | 0.44699 (17) | 0.0219 (5) | 0.749 (4) |
| H8  | 0.906 (5) | 0.538 (3) | 0.3925 (16) | 0.033* 0.749 (4) |
| H8A | 0.960 (8) | 0.519 (4) | 0.478 (9) | 0.033* 0.251 (4) |
| H9  | 0.928 (4) | 0.5886 (13) | 0.458 (3) | 0.033* 0.251 (4) |
| O17 | 0.3486 (3) | 0.4558 (2) | 0.1490 (2) | 0.0263 (8) 0.749 (4) |
| H10 | 0.358 (5) | 0.4098 (12) | 0.151 (4) | 0.039* 0.749 (4) |
| H11 | 0.396 (6) | 0.475 (3) | 0.123 (5) | 0.039* 0.749 (4) |
| O17A | 0.731 (3) | 0.5080 (16) | 0.327 (2) | 0.0178 (12) 0.251 (4) |
| H10A | 0.796 (3) | 0.525 (6) | 0.338 (3) | 0.027* 0.251 (4) |
| H11A | 0.692 (6) | 0.538 (4) | 0.290 (6) | 0.027* 0.251 (4) |
| C1  | 0.6872 (3) | 0.71285 (17) | 0.4349 (2) | 0.0168 (6) |
| C2  | 0.7424 (3) | 0.7812 (2) | 0.3970 (2) | 0.0237 (7) |
| C3  | 0.3584 (3) | 0.65671 (18) | 0.2611 (2) | 0.0170 (6) |
| C4  | 0.3288 (3) | 0.7092 (2) | 0.1773 (2) | 0.0280 (8) |
| C7  | 0.2064 (3) | 0.65978 (18) | 0.5141 (2) | 0.0176 (6) |
| C8  | 0.1216 (3) | 0.7149 (2) | 0.5428 (2) | 0.0241 (7) |
| C9  | 0.5313 (3) | 0.71245 (18) | 0.6826 (2) | 0.0181 (6) |
| C10 | 0.5304 (3) | 0.7826 (2) | 0.7442 (2) | 0.0258 (7) |
| C11 | 0.8490 (3) | 0.55266 (18) | 0.6861 (2) | 0.0209 (7) |

**Atomic displacement parameters (Å²)**

|   | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|-------|-------|-------|-------|-------|-------|
| Yb1 | 0.01250 (6) | 0.01161 (6) | 0.01467 (7) | 0.00037 (4) | 0.00311 (5) | 0.00005 (4) |
| Yb2 | 0.01271 (7) | 0.01391 (7) | 0.01816 (7) | −0.00026 (4) | 0.00445 (5) | −0.00032 (5) |
| Yb3 | 0.01161 (7) | 0.01416 (7) | 0.01668 (7) | −0.00005 (4) | 0.00478 (5) | −0.00059 (5) |
| F1  | 0.0149 (8) | 0.0153 (8) | 0.0143 (8) | −0.0003 (7) | 0.0037 (7) | 0.0003 (7) |
| F2  | 0.0134 (8) | 0.0141 (8) | 0.0177 (9) | 0.0005 (7) | 0.0039 (7) | 0.0011 (7) |
| F3  | 0.0131 (8) | 0.0143 (8) | 0.0161 (9) | 0.0005 (6) | 0.0039 (7) | 0.0006 (6) |
| F4  | 0.0144 (8) | 0.0140 (8) | 0.0148 (8) | −0.0004 (7) | 0.0027 (7) | 0.0005 (7) |
| F5  | 0.100 (2) | 0.0670 (19) | 0.0231 (13) | −0.0320 (17) | 0.0179 (14) | 0.0085 (12) |
| F6  | 0.0210 (11) | 0.0392 (14) | 0.081 (2) | −0.0076 (10) | 0.0033 (12) | 0.0276 (13) |
| F7  | 0.0431 (14) | 0.0205 (11) | 0.0783 (19) | −0.0005 (10) | 0.0238 (14) | 0.0125 (11) |
| F8  | 0.051 (3) | 0.057 (3) | 0.056 (4) | 0.001 (2) | 0.034 (3) | 0.027 (3) |
| F9  | 0.039 (2) | 0.023 (2) | 0.027 (2) | 0.0093 (17) | 0.005 (2) | 0.0089 (15) |
| F10 | 0.072 (4) | 0.035 (2) | 0.016 (2) | 0.005 (2) | −0.006 (2) | 0.0019 (16) |
| F8A | 0.051 (8) | 0.061 (9) | 0.022 (8) | 0.014 (7) | −0.013 (6) | 0.004 (6) |
| F9A | 0.072 (8) | 0.067 (9) | 0.037 (7) | 0.005 (6) | 0.031 (6) | 0.022 (6) |
| F10A | 0.094 (15) | 0.027 (7) | 0.040 (8) | 0.009 (8) | 0.017 (11) | 0.016 (5) |
| F11 | 0.046 (3) | 0.134 (5) | 0.060 (3) | −0.020 (3) | 0.021 (3) | 0.031 (4) |
| F12 | 0.132 (7) | 0.055 (4) | 0.065 (5) | −0.014 (4) | 0.069 (5) | −0.016 (3) |
| F13 | 0.089 (4) | 0.062 (3) | 0.070 (4) | 0.027 (3) | 0.042 (3) | 0.045 (3) |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| O8 | 0.018 (4) | 0.029 (3) | 0.014 (3) | −0.002 (3) | 0.003 (3) |
| O9 | 0.016 (2) | 0.021 (4) | 0.017 (2) | 0.003 (2) | 0.0043 (15) |
| C5 | 0.022 (2) | 0.0148 (19) | 0.018 (2) | 0.0031 (16) | 0.0091 (17) |
| C6 | 0.023 (2) | 0.039 (3) | 0.029 (3) | 0.003 (2) | 0.014 (2) |
| F11A | 0.061 (7) | 0.059 (7) | 0.040 (6) | −0.001 (5) | 0.027 (5) |
| F12A | 0.119 (12) | 0.049 (7) | 0.097 (10) | 0.000 (7) | 0.073 (10) |
| F13A | 0.097 (10) | 0.098 (11) | 0.065 (9) | −0.032 (8) | 0.046 (8) |
| O8A | 0.018 (4) | 0.029 (3) | 0.014 (3) | −0.002 (3) | 0.003 (3) |
| O9A | 0.017 (6) | 0.024 (7) | 0.012 (6) | −0.002 (5) | 0.004 (5) |
| C5A | 0.047 (8) | 0.044 (7) | 0.032 (7) | −0.001 (5) | 0.003 (5) |
| C6A | 0.039 (7) | 0.057 (5) | 0.045 (5) | 0.021 (4) | 0.034 (4) |
| F12B | 0.068 (6) | 0.040 (5) | 0.037 (5) | −0.020 (4) | 0.025 (4) |
| F14 | 0.053 (16) | 0.0700 (19) | 0.0323 (13) | 0.0223 (14) | 0.0084 (12) |
| F15 | 0.053 (13) | 0.0237 (11) | 0.0648 (17) | 0.0139 (9) | 0.0218 (12) |
| F16 | 0.0192 (11) | 0.0327 (12) | 0.0807 (19) | 0.0015 (9) | 0.0185 (11) |
| F17 | 0.037 (2) | 0.064 (4) | 0.071 (4) | 0.017 (2) | 0.006 (2) |
| F18 | 0.053 (4) | 0.053 (3) | 0.033 (3) | −0.002 (3) | 0.004 (3) |
| C12 | 0.0169 (18) | 0.034 (3) | 0.023 (2) | 0.0023 (17) | 0.0010 (15) |
| F20 | 0.0298 (19) | 0.077 (3) | 0.053 (3) | −0.001 (2) | −0.0149 (18) |
| F21 | 0.0161 (17) | 0.094 (4) | 0.037 (2) | −0.005 (3) | 0.0057 (16) |
| F22 | 0.0268 (18) | 0.058 (3) | 0.063 (3) | −0.0015 (18) | −0.0120 (18) |
| C12A | 0.0169 (18) | 0.034 (3) | 0.023 (2) | 0.0023 (17) | 0.0010 (15) |
| F20A | 0.030 (7) | 0.070 (8) | 0.056 (7) | −0.029 (7) | −0.001 (5) |
| F21A | 0.031 (6) | 0.138 (13) | 0.029 (6) | 0.001 (8) | 0.007 (5) |
| F22A | 0.034 (6) | 0.045 (6) | 0.089 (9) | 0.014 (5) | −0.019 (6) |
| N1 | 0.035 (2) | 0.016 (4) | 0.033 (3) | 0.002 (2) | 0.008 (2) |
| O1 | 0.035 (2) | 0.016 (4) | 0.033 (3) | 0.002 (2) | 0.008 (2) |
| O2 | 0.061 (4) | 0.082 (4) | 0.050 (3) | −0.013 (4) | −0.013 (3) |
| O3 | 0.057 (3) | 0.067 (4) | 0.067 (5) | 0.002 (3) | −0.003 (4) |
| O2A | 0.061 (4) | 0.082 (4) | 0.050 (3) | −0.013 (4) | −0.013 (3) |
| O3A | 0.057 (3) | 0.067 (4) | 0.067 (5) | 0.002 (3) | −0.003 (4) |
| O4 | 0.0186 (11) | 0.0205 (12) | 0.0256 (12) | −0.0030 (9) | 0.0070 (10) |
| O5 | 0.0182 (11) | 0.0177 (11) | 0.0229 (12) | −0.0036 (9) | 0.0060 (9) |
| O6 | 0.0212 (11) | 0.0203 (11) | 0.0174 (11) | 0.0005 (9) | 0.0029 (9) |
| O7 | 0.0213 (11) | 0.0220 (12) | 0.0168 (11) | 0.0013 (9) | 0.0026 (9) |
| O10 | 0.0173 (11) | 0.0177 (11) | 0.0199 (11) | 0.0038 (9) | 0.0042 (9) |
| O11 | 0.0180 (11) | 0.0182 (11) | 0.0300 (13) | 0.0015 (9) | 0.0097 (10) |
| O12 | 0.0192 (11) | 0.0175 (11) | 0.0184 (11) | −0.0010 (9) | 0.0033 (9) |
| O13 | 0.0231 (12) | 0.0208 (12) | 0.0178 (11) | −0.0013 (9) | 0.0031 (9) |
| O14 | 0.0181 (11) | 0.0262 (12) | 0.0227 (12) | −0.0018 (9) | 0.0030 (9) |
| O15 | 0.0163 (11) | 0.0228 (12) | 0.0206 (12) | −0.0024 (9) | 0.0010 (9) |
|     | 0.0165 (11) | 0.0257 (12) | 0.0236 (13) | −0.0030 (10) | 0.0043 (10) | −0.0022 (10) |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| O16 | 0.0266 (18) | 0.0310 (18) | 0.0194 (17) | −0.0003 (15) | 0.0009 (15) | −0.0031 (14) |
| O17 | 0.016 (2)   | 0.021 (4)   | 0.017 (2)   | 0.003 (2)    | 0.0043 (15) | 0.000 (2)    |
| O17A| 0.0202 (15) | 0.0158 (14) | 0.0131 (14) | −0.0061 (12) | 0.0013 (12) | −0.0008 (11) |
| C1  | 0.0206 (16) | 0.0244 (17) | 0.0257 (18) | −0.0033 (13) | 0.0046 (14) | 0.0070 (13)  |
| C2  | 0.0121 (14) | 0.0215 (16) | 0.0171 (15) | 0.0013 (12)  | 0.0031 (12) | 0.0047 (12)  |
| C3  | 0.037 (2)   | 0.0267 (18) | 0.0210 (17) | 0.0025 (15)  | 0.0070 (15) | 0.0056 (14)  |
| C4  | 0.0156 (15) | 0.0197 (15) | 0.0167 (15) | 0.0035 (12)  | 0.0020 (12) | −0.0027 (12) |
| C7  | 0.0190 (16) | 0.0241 (17) | 0.0289 (18) | 0.0024 (13)  | 0.0048 (14) | −0.0065 (14) |
| C8  | 0.0154 (14) | 0.0196 (15) | 0.0196 (16) | −0.0035 (12) | 0.0045 (12) | −0.0036 (12) |
| C9  | 0.0313 (19) | 0.0241 (17) | 0.0215 (17) | 0.0025 (14)  | 0.0046 (14) | −0.0034 (13) |
| C10 | 0.0179 (16) | 0.0179 (15) | 0.0236 (17) | −0.0011 (12) | −0.0026 (13) | −0.0017 (13) |

**Geometric parameters (Å, °)**

| Bond/Distance | Yb1-F1 | F14-C8 | 1.317 (4) |
|---------------|--------|--------|-----------|
| Yb1-F2       | 2.2375 (17) | F15-C8 | 1.327 (4) |
| Yb1-F3       | 2.2382 (17) | F16-C8 | 1.321 (4) |
| Yb1-F4       | 2.2431 (17) | F17-C10 | 1.305 (5) |
| Yb1-O5       | 2.2444 (17) | F18-C10 | 1.342 (5) |
| Yb1-O10      | 2.273 (2) | F19-C10 | 1.305 (5) |
| Yb1-O6       | 2.291 (2) | F19-C10 | 1.305 (6) |
| Yb1-O12      | 2.306 (2) | F17A-C10 | 1.316 (7) |
| Yb2-O8A      | 2.309 (2) | F18A-C10 | 1.313 (7) |
| Yb2-O15      | 2.223 (4) | F19A-C10 | 1.297 (7) |
| Yb2-O13      | 2.286 (2) | C12-F21 | 1.315 (7) |
| Yb2-O14      | 2.2895 (17) | C12-F22 | 1.316 (7) |
| Yb2-O17      | 2.299 (13) | C12-F20 | 1.326 (8) |
| Yb2-O11      | 2.303 (2) | C12-C11 | 1.549 (6) |
| Yb2-O16      | 2.3035 (17) | C12A-F20A | 1.296 (18) |
| Yb2-F1       | 2.3061 (17) | C12A-F22A | 1.301 (18) |
| Yb2-O17A     | 2.3276 (17) | C12A-F21A | 1.302 (18) |
| Yb3-O13      | 2.329 (2) | C12A-C11 | 1.531 (15) |
| Yb3-O17      | 2.544 (3) | N1-H12 | 0.9100 |
| Yb3-O11      | 3.054 (11) | N1-H13 | 0.9100 |
| Yb3-O17A     | 2.27 (4) | N1-H14 | 0.9099 |
| Yb3-O14      | 2.290 (2) | N1-H15 | 0.9099 |
| Yb3-O9       | 2.312 (11) | O1-H1 | 0.8400 |
| Yb3-O11      | 2.321 (2) | O1-H2 | 0.8401 |
| Yb3-O3       | 2.3210 (17) | O1-H3 | 0.8401 |
| Yb3-O4       | 2.323 (2) | O2-H4 | 0.830 (2) |
| Yb3-F2       | 2.3321 (17) | O2-H5 | 0.830 (2) |
| Yb3-F1       | 2.3321 (17) | O3-H6 | 0.852 (17) |
| Yb3-F4       | 2.3509 (17) | O3-H7 | 0.849 (18) |
| Yb3-O16      | 2.448 (2) | O2A-H4A | 0.830 (2) |
| F5-C2        | 1.306 (4) | O2A-H5A | 0.830 (3) |
| F6-C2        | 1.312 (4) | O3A-H6A | 0.83 (2) |
| F7-C2        | 1.327 (4) | O3A-H7A | 0.84 (2) |
| F8-C4        | 1.322 (6) | O4-C1 | 1.244 (4) |
| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| F9—C4         | 1.341 (6)    | O5—C1         | 1.246 (4)    |
| F10—C4        | 1.333 (6)    | O6—C3         | 1.244 (4)    |
| F8A—C4        | 1.315 (14)   | O7—C3         | 1.239 (4)    |
| F9A—C4        | 1.302 (14)   | O10—C7        | 1.248 (4)    |
| F10A—C4       | 1.311 (15)   | O11—C7        | 1.236 (4)    |
| F11—C6        | 1.317 (2)    | O12—C9        | 1.246 (4)    |
| F12—C6        | 1.319 (2)    | O13—C9        | 1.239 (4)    |
| F13—C6        | 1.315 (2)    | O14—C11       | 1.231 (4)    |
| O8—C5         | 1.240 (10)   | O15—C11       | 1.251 (4)    |
| O9—C5         | 1.250 (11)   | O16—H8        | 0.831 (19)   |
| C5—C6         | 1.519 (6)    | O16—H8A       | 0.84 (2)     |
| F11A—C6A      | 1.320 (2)    | O16—H9        | 0.817 (19)   |
| F12A—C6A      | 1.320 (2)    | O17—H10       | 0.81 (2)     |
| F13A—C6A      | 1.320 (2)    | O17—H11       | 0.84 (2)     |
| O8A—C5A       | 1.26 (4)     | O17A—H10A     | 0.830 (2)    |
| O9A—C5A       | 1.207 (17)   | O17A—H11A     | 0.830 (2)    |
| C5A—C6A       | 1.532 (14)   | C1—C2         | 1.544 (4)    |
| C6B—F11B      | 1.266 (14)   | C3—C4         | 1.545 (5)    |
| C6B—F12B      | 1.318 (11)   | C7—C8         | 1.544 (4)    |
| C6B—F13B      | 1.355 (12)   | C9—C10        | 1.546 (4)    |
| F1—Yb1—F2     | 68.51 (6)    | Yb1—F4—Yb2   | 111.42 (7)   |
| F1—Yb1—F3     | 68.68 (6)    | Yb1—F4—Yb3   | 112.27 (7)   |
| F2—Yb1—F3     | 105.52 (6)   | Yb2—F4—Yb3   | 115.81 (7)   |
| F1—Yb1—F4i    | 105.62 (6)   | C5—O8—Yb2    | 135.7 (7)    |
| F2—Yb1—F4i    | 68.79 (6)    | C5—O9—Yb3    | 136.4 (7)    |
| F3—Yb1—F4i    | 68.20 (6)    | O8—C5—O9     | 129.5 (8)    |
| F1—Yb1—O5     | 79.54 (7)    | O8—C5—C6     | 114.2 (6)    |
| F2—Yb1—O5     | 79.72 (7)    | O9—C5—C6     | 116.3 (6)    |
| F3—Yb1—O5     | 142.37 (7)   | F13—C6—F11   | 107.9 (5)    |
| F4—Yb1—O5     | 142.72 (7)   | F13—C6—F12   | 107.5 (6)    |
| F1—Yb1—O10    | 142.97 (7)   | F11—C6—F12   | 106.4 (6)    |
| F2—Yb1—O10    | 141.71 (7)   | F13—C6—C5    | 110.7 (4)    |
| F3—Yb1—O10    | 79.93 (7)    | F11—C6—C5    | 114.2 (4)    |
| F4—Yb1—O10    | 79.02 (7)    | F12—C6—C5    | 109.9 (6)    |
| O5—Yb1—O10    | 119.28 (8)   | C5A—O8A—Yb2  | 120 (2)      |
| F1—Yb1—O6     | 79.31 (7)    | O9A—C5A—O8A  | 126 (2)      |
| F2—Yb1—O6     | 142.28 (7)   | O9A—C5A—C6A  | 120.0 (12)   |
| F3—Yb1—O6     | 79.24 (7)    | O8A—C5A—C6A  | 114 (2)      |
| F4—Yb1—O6     | 141.72 (7)   | O9A—C5A—Yb2  | 88.0 (8)     |
| O5—Yb1—O6     | 75.44 (8)    | C6A—C5A—Yb2  | 151.3 (8)    |
| O10—Yb1—O6    | 75.89 (8)    | F13A—C6A—F12A| 106.3 (11)   |
| F1—Yb1—O12    | 142.51 (7)   | F13A—C6A—F11A| 105.6 (11)   |
| F2—Yb1—O12    | 79.38 (7)    | F12A—C6A—F11A| 105.7 (9)    |
| F3—Yb1—O12    | 141.46 (7)   | F13A—C6A—C5A | 117.8 (13)   |
| F4—Yb1—O12    | 78.91 (7)    | F12A—C6A—C5A | 109.5 (10)   |
| O5—Yb1—O12    | 76.05 (8)    | F11A—C6A—C5A | 111.1 (10)   |
| O10—Yb1—O12   | 74.46 (8)    | F11B—C6B—F12B| 108.8 (9)    |
| Bond                | Angle (°) | Error (°) |
|---------------------|-----------|-----------|
| O6—Yb1—O12         | 120.44    | (8)       |
| O8A—Yb2—O15i       | 122.8     | (7)       |
| O15i—Yb2—F2        | 77.45     | (7)       |
| O15i—Yb2—O8        | 130.11    | (18)      |
| F2—Yb2—O8          | 141.6     | (3)       |
| O8A—Yb2—O7         | 78.4      | (11)      |
| O15i—Yb2—O7        | 81.21     | (8)       |
| F2—Yb2—O7          | 137.25    | (7)       |
| O8—Yb2—O7          | 79.2      | (3)       |
| O8A—Yb2—F4         | 82.4      | (9)       |
| O15—Yb2—F4         | 140.92    | (7)       |
| F2—Yb2—F4          | 66.91     | (6)       |
| O8—Yb2—F4          | 77.2      | (3)       |
| O7—Yb2—F4          | 136.54    | (7)       |
| O8A—Yb2—F3         | 142.9     | (10)      |
| O15—Yb2—F3         | 78.19     | (7)       |
| F2—Yb2—F3          | 64.51     | (6)       |
| O8—Yb2—F3          | 137.7     | (3)       |
| O7—Yb2—F3          | 75.12     | (7)       |
| F4—Yb2—F3          | 99.50     | (6)       |
| O8A—Yb2—F1         | 82.3      | (8)       |
| O15—Yb2—F1         | 140.92    | (7)       |
| F2—Yb2—F1          | 99.78     | (6)       |
| O8—Yb2—F1          | 75.12     | (19)      |
| O7—Yb2—F1          | 74.92     | (7)       |
| F4—Yb2—F1          | 64.05     | (6)       |
| F3—Yb2—F1          | 66.11     | (6)       |
| O15i—Yb2—O13i      | 81.76     | (8)       |
| F2—Yb2—O13i        | 76.31     | (7)       |
| O8—Yb2—O13i        | 81.8      | (3)       |
| O7—Yb2—O13i        | 136.28    | (8)       |
| F4—Yb2—O13i        | 74.85     | (7)       |
| F3—Yb2—O13i        | 138.88    | (7)       |
| F1—Yb2—O13i        | 136.15    | (7)       |
| O15i—Yb2—O17       | 65.63     | (10)      |
| F2—Yb2—O17         | 131.62    | (10)      |
| O8—Yb2—O17         | 64.50     | (19)      |
| O7—Yb2—O17         | 67.64     | (10)      |
| F4—Yb2—O17         | 129.63    | (9)       |
| F3—Yb2—O17         | 130.81    | (9)       |
| F1—Yb2—O17         | 128.60    | (9)       |
| O13i—Yb2—O17       | 68.65     | (10)      |
| O8A—Yb2—C5A        | 20.9      | (8)       |
| O15i—Yb2—C5A       | 101.9     | (2)       |
| F2—Yb2—C5A         | 149.4     | (2)       |
| O7—Yb2—C5A         | 71.3      | (2)       |
| F4—Yb2—C5A         | 100.8     | (2)       |
| F3—Yb2—C5A         | 145.9     | (2)       |

*Acta Cryst. (2022). E78, 608-614*
| Bond          | Distance (Å) | Angle (°)   | Torsion (°) |
|--------------|--------------|-------------|-------------|
| F1—Yb2—C5A  | 99.1 (2)     | O4—C1—O5   | 129.6 (3)   |
| O13—Yb2—C5A | 73.4 (2)     | O4—C1—C2   | 115.3 (3)   |
| O17A—Yb3—O14| 133.8 (9)    | O5—C1—C2   | 115.0 (3)   |
| O14—Yb3—O9  | 135.5 (3)    | F5—C2—F6   | 109.2 (3)   |
| O14—Yb3—O11i| 82.90 (8)    | F5—C2—F7   | 106.5 (3)   |
| O9—Yb3—O11i | 84.38 (16)   | F6—C2—F7   | 106.3 (3)   |
| O14—Yb3—F3i | 74.74 (7)    | F5—C2—C1   | 109.5 (3)   |
| O9—Yb3—F3i  | 141.5 (2)    | F6—C2—C1   | 112.9 (3)   |
| O11i—Yb3—F3i| 75.69 (7)    | F7—C2—C1   | 112.1 (3)   |
| O17A—Yb3—O4 | 85.1 (7)     | O7—C3—C4   | 114.6 (3)   |
| O14—Yb3—O4  | 84.13 (9)    | O7—C3—C4   | 114.6 (3)   |
| O9—Yb3—O4   | 78.74 (19)   | O6—C3—C4   | 115.1 (3)   |
| O11i—Yb3—O4 | 139.80 (8)   | F9A—C4—F10A| 108.5 (11)  |
| F3i—Yb3—O4  | 136.04 (7)   | F9A—C4—F8A | 106.7 (9)   |
| O17A—Yb3—F2 | 141.7 (7)    | F10A—C4—F8A| 107.9 (11)  |
| O14—Yb3—F2  | 76.44 (7)    | F8—C4—F10  | 108.0 (4)   |
| O9—Yb3—F2   | 135.08 (17)  | F8—C4—F9   | 107.7 (4)   |
| O11i—Yb3—F2 | 137.83 (7)   | F10—C4—F9  | 106.6 (5)   |
| F3i—Yb3—F2  | 63.63 (6)    | F9A—C4—C3  | 111.9 (9)   |
| O4—Yb3—F2   | 74.24 (7)    | F10A—C4—C3 | 114.5 (12)  |
| O17A—Yb3—F1 | 78.4 (8)     | F8A—C4—C3  | 107.0 (10)  |
| O14—Yb3—F1  | 140.07 (7)   | F8—C4—C3   | 109.0 (4)   |
| O9—Yb3—F1   | 73.3 (2)     | F10—C4—C3  | 113.1 (4)   |
| O11i—Yb3—F1 | 133.95 (7)   | F9—C4—C3   | 112.2 (4)   |
| F3i—Yb3—F1  | 97.34 (6)    | O11—C7—O10 | 130.0 (3)   |
| O4—Yb3—F1   | 74.91 (7)    | O11—C7—C8  | 115.3 (3)   |
| F2—Yb3—F1   | 65.39 (6)    | O10—C7—C8  | 114.6 (3)   |
| O17A—Yb3—F4 | 74.9 (9)     | F14—C8—F16 | 107.6 (3)   |
| O14—Yb3—F4  | 136.97 (7)   | F14—C8—F15 | 107.5 (3)   |
| O9—Yb3—F4   | 77.7 (2)     | F16—C8—F15 | 107.1 (3)   |
| O11i—Yb3—F4 | 72.99 (7)    | F14—C8—C7  | 109.4 (3)   |
| F3i—Yb3—F4  | 65.16 (6)    | F16—C8—C7  | 112.3 (3)   |
| O4—Yb3—F4   | 136.25 (7)   | F15—C8—C7  | 112.8 (3)   |
| F2—Yb3—F4   | 98.13 (6)    | O13—C9—O12 | 129.9 (3)   |
| F1—Yb3—F4   | 63.25 (6)    | O13—C9—C10 | 115.8 (3)   |
| O17A—Yb3—O16| 65.8 (9)     | O12—C9—C10 | 114.3 (3)   |
| O14—Yb3—O16 | 68.32 (8)    | F19—C10—F17| 108.5 (5)   |
| O9—Yb3—O16  | 67.3 (3)     | F19A—C10—F18A| 108.5 (6) |
| O11i—Yb3—O16| 69.60 (8)    | F19A—C10—F17A| 107.1 (6) |
| F3i—Yb3—O16 | 131.44 (7)   | F18A—C10—F17A| 106.6 (6) |
| O4—Yb3—O16  | 70.24 (8)    | F19—C10—F18 | 105.9 (5)   |
| F2—Yb3—O16  | 131.62 (7)   | F17—C10—F18 | 105.6 (4)   |
| F1—Yb3—O16  | 131.20 (7)   | F19A—C10—C9 | 114.2 (4)   |
| F4—Yb3—O16  | 130.25 (7)   | F19—C10—C9  | 114.2 (3)   |
| Yb1—F1—Yb2  | 111.91 (7)   | F17—C10—C9  | 112.0 (3)   |
| Yb1—F1—Yb3  | 112.59 (7)   | F18A—C10—C9 | 109.5 (4)   |
| Yb2—F1—Yb3  | 115.60 (7)   | F17A—C10—C9 | 110.7 (4)   |
| Yb1—F2—Yb2  | 112.17 (7)   | F18—C10—C9  | 110.2 (3)   |
Yb1—F2—Yb3 112.58 (7) O14—C11—O15 129.8 (3)
Yb2—F2—Yb3 115.21 (7) O14—C11—C12A 110.5 (8)
Yb1—F3—Yb2 112.51 (7) O15—C11—C12A 119.4 (8)
Yb1—F3—Yb3 113.46 (7) O14—C11—C12 117.3 (4)
Yb2—F3—Yb3 114.98 (7) O15—C11—C12 112.9 (4)

Symmetry code: (i) −x+1, −y+1, −z+1.

Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A | D—H···A |
|-------------|-----|-------|-------|---------|
| N1—H12···O6 | 0.91| 2.21  | 2.883 (8) | 131      |
| N1—H15···O17ii | 0.91| 1.86  | 2.766 (7) | 172      |
| N1—H13···O10 | 0.91| 2.08  | 2.853 (10) | 142     |
| N1—H14···O2  | 0.91| 1.95  | 2.837 (9) | 165      |
| O1—H2···O2A | 0.84| 1.78  | 2.619 (18) | 175      |
| O1—H3···O9Aiii | 0.84| 2.01  | 2.842 (16) | 173      |
| O1—H1···O10 | 0.84| 2.30  | 3.03 (3) | 145      |
| O2—H4···O3  | 0.83 (1)| 1.91 (3) | 2.704 (11) | 159 (7) |
| O2—H5···O12 | 0.83 (1)| 2.31 (5) | 2.978 (7) | 138 (6) |
| O3—H6···O2iii | 0.85 (2)| 2.22 (2) | 3.055 (10) | 167 (8) |
| O3—H7···O17iv | 0.85 (2)| 2.01 (2) | 2.835 (9) | 163 (8) |
| O2A—H4A···F19A | 0.83 (1)| 1.90 (7) | 2.68 (2) | 156 (17) |
| O2A—H5A···O3Aiii | 0.83 (1)| 2.35 (14) | 2.96 (3) | 131 (16) |
| O3A—H7A···O2A | 0.84 (2)| 2.20 (15) | 2.91 (4) | 143 (23) |
| O3A—H6A···O9Aiv | 0.83 (2)| 2.6 (2) | 3.03 (4) | 115 (19) |
| O16—H8···O9  | 0.83 (2)| 2.28 (6) | 2.639 (10) | 107 (4) |
| O16—H8···O16v | 0.84 (2)| 2.07 (2) | 2.903 (5) | 179 (17) |
| O16—H9···F16vi | 0.82 (2)| 2.17 (2) | 2.954 (3) | 160 (4) |
| O17—H11···O8  | 0.84 (2)| 2.25 (8) | 2.593 (7) | 105 (7) |
| O17—H10···O13i | 0.81 (2)| 2.22 (5) | 2.754 (4) | 123 (5) |
| O17A—H10A···O16 | 0.83 (1)| 1.92 (2) | 2.56 (3) | 134 (5) |

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) −x+1/2, −y+1/2, −z+1/2; (iii) −x+1, −y+2, −z+1; (iv) x+1/2, −y+3/2, z+1/2; (v) −x+2, −y+1, −z+1; (vi) x+1, y, z.