

Structure of triaquatris(1,1,1-trifluoro-4-oxopentan-2-olato)cerium(III) as a possible fluorescent compound

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Received 1 December 2017

Accepted 17 January 2018

Edited by A. Van der Lee, Université de Montpellier II, France

Keywords: crystal structure; 1,1,1-trifluoroacetylacetone; cerium complex; fluorescence.

CCDC reference: 1817747

Supporting information: this article has supporting information at journals.iucr.org/e

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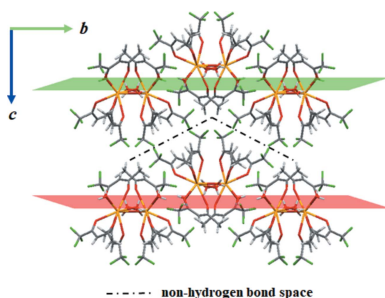
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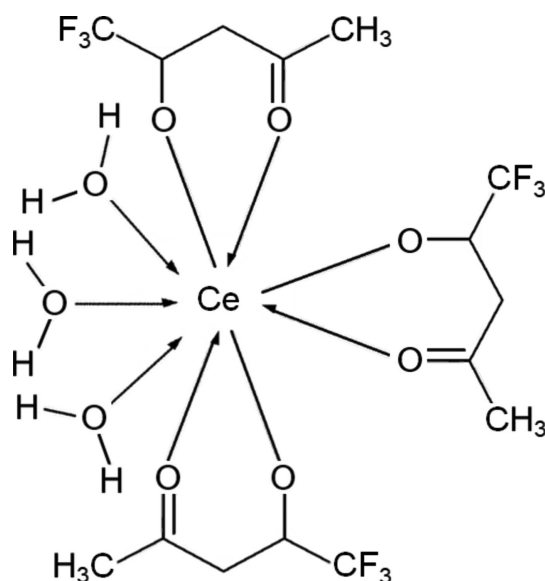
Luminescence due to the $d-f$ transition of Ce^{3+} is quite rare in metal–organic complexes where concentrate quenching frequently occurs. One of the possible ways to avoid this is to design an architecture with elongated metal–metal distances. In the structure of the title complex, triaquatris(1,1,1-trifluoro-4-oxopentan-2-olato- κ^2O,O')cerium(III), $[Ce(C_5H_4F_3O_2)_3(H_2O)_3]$, the Ce^{III} complex is linked to neighbouring ones by hydrogen bonding. Within the complex, the Ce^{III} atom is coordinated by nine O atoms from three 1,1,1-trifluoro-4-oxopentan-2-olate (tfa) anions as bidentate ligands and three water molecules as monodentate ligands. Thus, the coordination number of Ce^{III} atom is nine in a monocapped square–antiprismatic polyhedron. The F atoms of all three independent CF_3 groups in tfa are disordered over two positions with occupancy ratios of about 0.8:0.2. The intermolecular hydrogen bonds between the ligands involve tfa–water interactions along the $[110]$ and $[1\bar{1}0]$ directions, generating an overall two-dimensional layered network structure. The presence of the F atoms in the tfa anion is responsible for an increased intermolecular metal–metal distance compared to that in the analogous acetylacetonate (acac) derivatives. Fluorescence from Ce^{3+} is, however, not observed.

1. Chemical context

β -diketonate ligands have been used widely in metal–organic complexes involving rare earth elements because of their simple usage as organic bidentate ligands (Binnemans, 2005). The nature of the ligand used is important for a possible enhancement of the luminescence efficiency and intensity; for example, acac is known to have a possible effect on the $4f-4f$ transition emission of Eu^{3+} (Kuz'mina *et al.*, 2006). $Tb(acac)_3$ was first used as an active light-emitting layer material in LEDs based on the emission from the lanthanide complex (Kido *et al.*, 1990). Recently, a lanthanide complex containing Tb^{3+} and Eu^{3+} , hexafluoroacetylacetonate (hfa) and 4,4'-bis(-diphenylphosphoryl)biphenyl (dpdp), $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpdp)]_n$, was reported to exhibit an expression thermo-sensing emission, called *chameleon* luminophore (Miyata *et al.*, 2013; Hasegawa & Nakanishi, 2015). The hfa anion can absorb efficiently a visible light excitation and transfer the



excited energy from hfa to Tb^{3+} , because the energy of the triplet state of hfa ($22\,000\text{ cm}^{-1}$) is very close to an energy level of Tb^{3+} ($20\,500\text{ cm}^{-1}$; Katagiri *et al.*, 2004). However, the proximity of the levels causes a back-energy transfer from Tb^{3+} to hfa. The probability of three types of energy transfer from hfa to Tb^{3+} , from Tb^{3+} to Eu^{3+} and from Tb^{3+} to hfa is temperature dependent. As a result, the complex can show green, yellow, orange and red emissions despite the $4f-4f$ transition.



The nature of the ligand is important in the design of fluorescent metal–organic complexes. The F atoms in hfa are larger than the H atoms in acac, which means that the hfa ligand can reduce the energy loss due to thermal vibrations and could increase the intermolecular distance between the central lanthanide atoms. This may control the concentration quenching.

A considerable number of metal–organic complexes containing Ce^{3+} have been reported so far, but the examples of emission based on the $5d-4f$ transition of Ce^{3+} in metal–organic complexes are scarce. $[Ce(\text{triRNTB})_2](CF_3SO_3)_3$ [NTB = *N*-substituted tris(*N*-alkylbenzimidazol-2-ylmethyl)-amine] and $[\infty^3[Ce(\text{Im})_3(\text{ImH})]\cdot\text{ImH}]$ (Zheng *et al.*, 2007; Meyer *et al.*, 2015) are some of the rare cases. One of the reasons for the small number of fluorescent metal–organic complexes containing Ce^{3+} is the too short distance between the Ce^{3+} ions, causing luminescence quenching by the energy transfer between Ce^{3+} ions. $[Ce(\text{triRNTB})_2](CF_3SO_3)_3$ can show a blue emission thanks to a long Ce–Ce distance of about 17–18 Å. The use of more bulky ligands such as NTB is favourable for a longer Ce–Ce distance. $[\infty^3[Ce(\text{Im})_3(\text{ImH})]\cdot\text{ImH}]$ also shows a blue fluorescence emission despite a relatively short separation between the Ce^{3+} cations of 7 Å. Emission occurs more frequently in 3D structures with isolated complexes than in framework structures.

This study reports structural data on a newly synthesized Ce^{3+} complex with functional ligands of tfa.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1W-H1WA\cdots O32^i$	0.84 (2)	2.13 (3)	2.927 (4)	158 (5)
$O1W-H1WB\cdots O22^i$	0.83 (2)	2.23 (4)	2.969 (4)	149 (6)
$O2W-H2WA\cdots O14^{ii}$	0.85 (2)	1.91 (2)	2.759 (4)	177 (6)
$O3W-H3WA\cdots O24^{iii}$	0.85 (2)	1.94 (2)	2.792 (4)	176 (7)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z$.

2. Structural commentary

The title complex crystallizes in the orthorhombic space group *Pcab* with eight formula units of $[Ce(C_5F_3H_4O_2)_3(H_2O)_3]$. Each molecule is isolated individually, *i.e.* the crystal structure is not a framework structure. The central Ce atom is coordinated by nine O atoms of three hfa and three water molecules (Fig. 1). Thus, the Ce atom has a monocapped square–antiprismatic coordination. The Ce–O bond lengths can be classified into two categories; the first is involved in interactions with a bidentate hfa, and the second in interactions with monodentate water molecules. All distances are comparable with those reported for tfa complexes (Nakamura *et al.*, 1986). The trifluoromethyl groups of tfa coordinating the Ce^{3+} ion are all disordered on the F atoms, as is frequently observed in trifluoroacetate and tetrafluoroborate complexes (Hamaguchi *et al.*, 2011; Strehler *et al.*, 2015).

3. Supramolecular features

The individual complexes are linked to neighbouring ones by four types of hydrogen bonds (Table 1), nearly within the *ab* plane. There are two types of hydrogen-bond directions; the first are parallel to $[110]$ and the second are parallel to $[1\bar{1}0]$. The chains consisting of the complex molecules and the

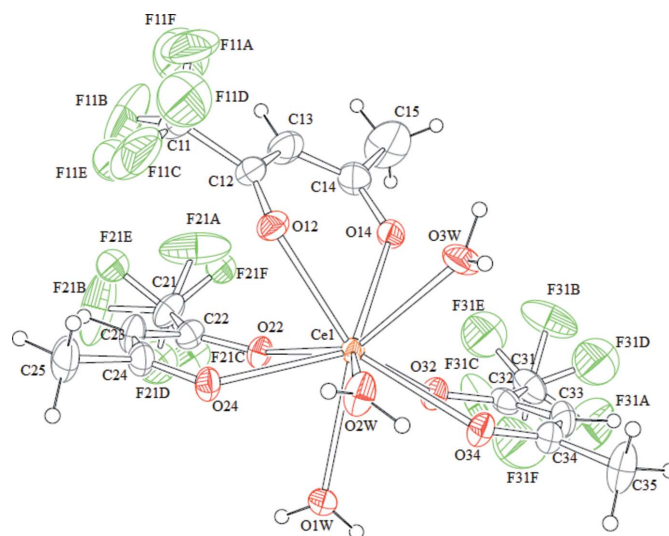


Figure 1
View of the molecular structure of the title complex, with displacement ellipsoids for non-H atoms drawn at the 30% probability level.

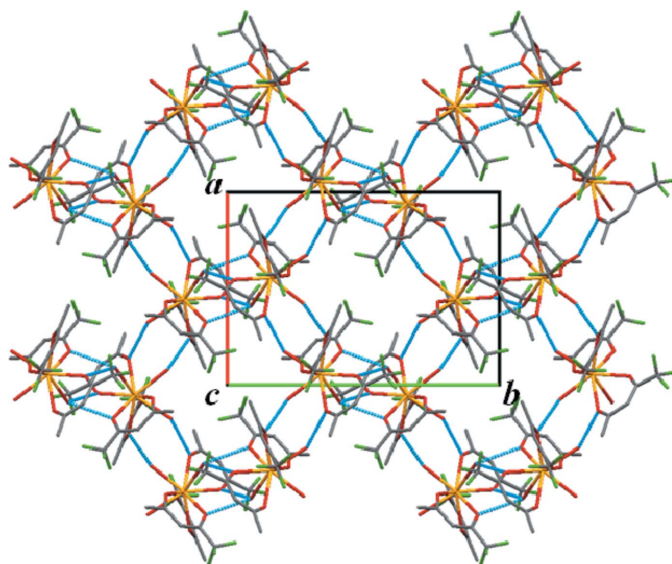


Figure 2
Connection of discrete complexes by intermolecular hydrogen-bonded (blue lines) chains in the *ab* plane, viewed in projection along the *c* axis. Colour code: Ce yellow, C grey, F green and O red. H atoms have been omitted. Only the major components of the disordered CF_3 groups are shown for clarity.

hydrogen bonds, two types of which are cross-linked to each other, building up two-dimensional networks (Fig. 2). The functional hydrophobic groups of $-\text{CF}_3$ and $-\text{CH}_3$ are located on the outside of the layer, resulting in the stabilization of the stacking layers by intermolecular forces. Such a layer structure is also observed in the acetylacetonate complex, $[\text{Y}(\text{C}_5\text{H}_7\text{O}_2)_3(\text{H}_2\text{O})_3]$ (Cunningham *et al.*, 1967) (Fig. 3). This yttrium complex also contains an isolated water in the structure, different from the title compound, but the water molecule can act as a hydrogen-bond linker because it exists within a molecular layer. As a result, the hydrogen bonds make a two-dimensional layered network, as in the title compound. The $Ln-Ln$ distance of nearest neighbours in this complex is longer than that of $[\text{Y}(\text{C}_5\text{H}_7\text{O}_2)_3(\text{H}_2\text{O})_3]$, the shortest distance in the former being 6.141 Å and in the latter 6.035 Å. This difference is mainly caused by atomic size difference between F and H atoms, even taking into account the atomic size difference between La and Y. The shortest $Ln-Ln$ distance of $[\text{La}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_3\text{H}_4\text{N}_2)(\text{NO}_3)(\text{H}_2\text{O})_2]$ (6.247 Å; Koizumi *et al.*, 2017) is slightly longer than that of the title compound. The fact that the present complex does not show any luminescence from Ce^{3+} can certainly be attributed to an insufficient metal-metal separation. Based on previous studies and the present work, the minimum metal-metal separation is expected to be more than 7 Å.

4. Database survey

Crystal structures of related complexes involving lanthanide ions have been reported with acac ligands (Berg & Acosta, 1968; Binnemans, 2005; Filotti *et al.*, 1996; Fujinaga *et al.*, 1981; Lim *et al.*, 1996; Phillips *et al.*, 1968; Richardson *et al.*, 1968; Stites *et al.*, 1948), with tfa complexes (Ilmi *et al.*, 2015;

Katagiri *et al.*, 2007; Li *et al.*, 2017; Lim *et al.*, 1996; Nakamura *et al.*, 1986; Yan *et al.*, 2009) and with hfa complexes (Subhan *et al.*, 2014; Fratini *et al.*, 2008; Hasegawa *et al.*, 2013, 2015; Kataoka *et al.*, 2016; Rybkin *et al.*, 2011; Tsaryuk *et al.*, 2017; Wang *et al.*, 2017; Yuasa *et al.*, 2011).

5. Synthesis and crystallization

Yellow plate-like crystals were obtained by slow evaporation from an acetone solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and trifluoroacetylacetonate (1:3 molar ratio). The products were filtered off and dried at room temperature.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms bonded to a C atom were positioned geometrically after each cycle in idealized locations and refined as riding on their parent C atoms with $\text{C}-\text{H} = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C atom})$. All hydrogen atoms bonded to a water O atom were located in a difference-Fourier map and refined isotropically with a distance restraint of 0.85 (2) Å and with thermal restraints $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{O atom})$. The occupancies of the disordered F atoms in the $-\text{CF}_3$

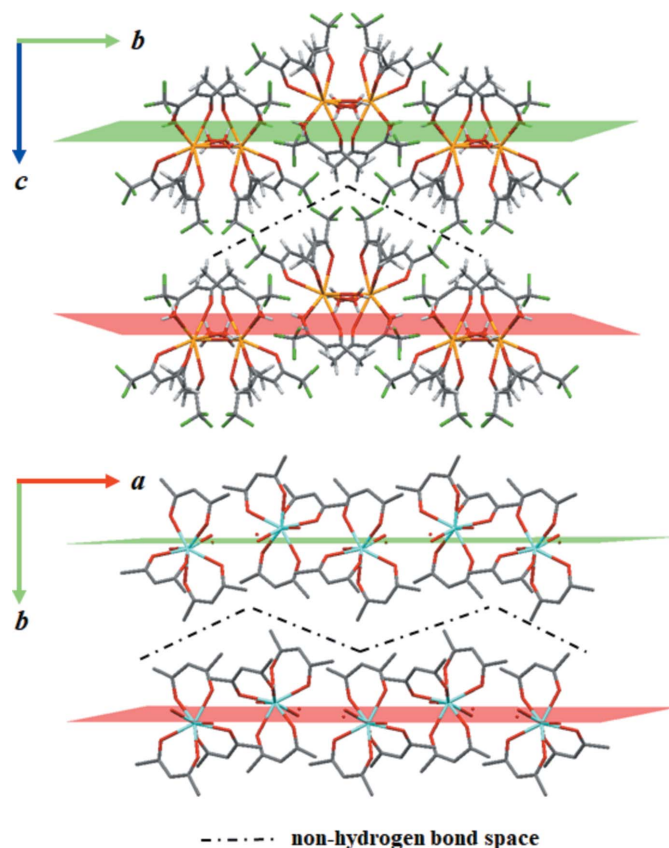


Figure 3
Comparison of the layered structures of the title compound and that of the $[\text{Y}(\text{C}_5\text{H}_7\text{O}_2)_3(\text{H}_2\text{O})_3]$ complex (Cunningham *et al.*, 1967). Colour code: Ce yellow, Y light blue, C grey, F green and O red. H atoms have been omitted. Only the main components of the disordered CF_3 groups are shown for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	[Ce(C ₅ H ₄ F ₃ O ₂) ₃ (H ₂ O) ₃]
<i>M</i> _r	653.41
Crystal system, space group	Orthorhombic, <i>Pcab</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.6347 (7), 16.5121 (9), 24.5577 (17)
<i>V</i> (Å ³)	4717.9 (5)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.04
Crystal size (mm)	0.3 × 0.19 × 0.11
Data collection	
Diffractometer	Rigaku XtaLAB mini
Absorption correction	Multi-scan (<i>REQAB</i> ; Rigaku, 1998)
<i>T</i> _{min} , <i>T</i> _{max}	0.603, 0.805
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	45156, 5404, 4309
<i>R</i> _{int}	0.039
(sin θ/λ) _{max} (Å ⁻¹)	0.649
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.092, 1.11
No. of reflections	5404
No. of parameters	367
No. of restraints	60
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.78, -0.44

Computer programs: *CrystalClear* (Rigaku, 2006) and *SORTAV* (Blessing, 1995), *SIR2014* (Burla *et al.*, 2015), *SHELXL2014* (Sheldrick, 2015) and *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012).

group were refined for the pairs F11A/F11D, F11B/F11E and F11C/F11F to be 0.829 (14)/0.171 (14), for the pairs of F21A/F21F, F21B/F21E and F21C/F21F to be 0.838 (17)/0.162 (17), and for the pairs of F31A/F31D, F31B/F31E and F31C/F31F to be 0.836 (11)/0.164 (11).

Funding information

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 17H03124 and No. 17H03386) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

Berg, E. W. & Acosta, J. J. C. (1968). *Anal. Chim. Acta*, **40**, 101–113.
 Binnemans, K. (2005). *Handbook on the Physics and Chemistry of Rare Earths* Vol. 35, edited by K. A. Gschneidner, J. C. G. Bunzli & V. K. Perchinsky, ch. 225, pp. 107–272. Amsterdam: Elsevier.
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Burla, M. C., Caliandro, R., Carrozzini, B., Cascarano, G. L., Cuocci, C., Giacovazzo, C., Mallamo, M., Mazzone, A. & Polidori, G. (2015). *J. Appl. Cryst.* **48**, 306–309.
 Cunningham, J. A., Sands, D. E. & Wagner, W. F. (1967). *Inorg. Chem.* **6**, 499–503.
 Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Filotti, L., Bugli, G., Ensuque, A. & Bozon-Verduraz, F. (1996). *Bull. Soc. Chim. Fr.* **133**, 1117–1126.
 Fratini, A., Richards, G., Larder, E. & Swavey, S. (2008). *Inorg. Chem.* **47**, 1030–1036.
 Fujinaga, T., Kuwamoto, T., Sugiura, K. & Ichiki, S. (1981). *Talanta*, **28**, 295–300.
 Hamaguchi, T., Nagata, T., Kawata, S. & Ando, I. (2011). *Acta Cryst.* **E67**, m1632.
 Hasegawa, Y. & Nakanishi, T. (2015). *RSC Adv.* **5**, 338–353.
 Hasegawa, Y., Ohkubo, T., Nakanishi, T., Kobayashi, A., Kato, M., Seki, T., Ito, H. & Fushimi, K. (2013). *Eur. J. Inorg. Chem.* pp. 5911–5918.
 Hasegawa, Y., Sato, N., Hirai, Y., Nakanishi, T., Kitagawa, Y., Kobayashi, A., Kato, M., Seki, T., Ito, H. & Fushimi, K. (2015). *J. Phys. Chem. A*, **119**, 4825–4833.
 Ilmi, R. & Iftikhar, K. (2015). *Polyhedron*, **102**, 16–26.
 Katagiri, S., Hasegawa, Y., Wada, Y. & Yanagida, S. (2004). *Chem. Lett.* **33**, 1438–1439.
 Katagiri, S., Tsukahara, Y., Hasegawa, Y. & Wada, Y. (2007). *Bull. Chem. Soc. Jpn.* **80**, 1492–1503.
 Kataoka, H., Nakanishi, T., Omagari, S., Takabatake, Y., Kitagawa, Y. & Hasegawa, Y. (2016). *Bull. Chem. Soc. Jpn.* **89**, 103–109.
 Kido, J., Nagai, K. & Ohashi, Y. (1990). *Chem. Lett.* **19**, 657–660.
 Koizumi, A., Hasegawa, T., Itadani, A., Toda, K., Zhu, T. & Sato, M. (2017). *Acta Cryst.* **E73**, 1739–1742.
 Kuz'mina, N. P. & Eliseeva, S. V. (2006). *Russ. J. Inorg. Chem.* **51**, 73–88.
 Li, H., Sun, J., Yang, M., Sun, Z., Xie, J., Ma, Y. & Li, L. (2017). *New J. Chem.* **41**, 10181–10188.
 Lim, J. T., Hong, S. T., Lee, J. C. & Lee, I. M. (1996). *Bull. Korean Chem. Soc.* **17**, 1023–1031.
 Meyer, L. V., Schönfeld, F., Zurawski, A., Mai, M., Feldmann, C. & Müller-Buschbaum, K. (2015). *Dalton Trans.* **44**, 4070–4079.
 Miyata, K., Konno, Y., Nakanishi, T., Kobayashi, A., Kato, M., Fushimi, K. & Hasegawa, Y. (2013). *Angew. Chem. Int. Ed.* **52**, 6413–6416.
 Nakamura, M., Nakamura, R., Nagai, K., Shimo, M., Tomoda, S., Takeuchi, Y. & Ouchi, A. (1986). *Bull. Chem. Soc. Jpn.* **59**, 332–334.
 Phillips, T. II, Sands, D. E. & Wagner, W. F. (1968). *Inorg. Chem.* **7**, 2295–2299.
 Richardson, M. F., Wagner, W. F. & Sands, D. E. (1968). *Inorg. Chem.* **7**, 2495–2500.
 Rigaku (1998). *REQAB*. Rigaku Corporation, Tokyo, Japan.
 Rigaku (2006). *CrystalClear-SM*. Rigaku Corporation, Tokyo, Japan.
 Rybkin, V. V., Tverdova, N. V., Girichev, G. V., Shlykov, S. A., Kuzmina, N. P. & Zaitseva, I. G. (2011). *J. Mol. Struct.* **1006**, 173–179.
 Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
 Stites, J. G., McCarty, C. N. & Quill, L. L. (1948). *J. Am. Chem. Soc.* **70**, 3142–3143.
 Strehler, F., Korb, M. & Lang, H. (2015). *Acta Cryst.* **E71**, 244–247.
 Subhan, M. A., Rahman, M. S., Alam, K. & Hasan, M. M. (2014). *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **118**, 944–950.
 Tsaryuk, V. I., Vologzhanina, A. V., Zhuravlev, K. P. & Kudryashova, V. A. (2017). *J. Fluor. Chem.* **197**, 87–93.
 Wang, Z., Liu, N. N., Li, H., Chen, P. & Yan, P. (2017). *Eur. J. Inorg. Chem.* pp. 2211–2219.
 Yan, B., Kong, L. L. & Zhou, B. (2009). *J. Non-Cryst. Solids*, **355**, 1281–1284.
 Yuasa, J., Ohno, T., Miyata, K., Tsumatori, H., Hasegawa, Y. & Kawai, T. (2011). *J. Am. Chem. Soc.* **133**, 9892–9902.
 Zheng, X. L., Liu, Y., Pan, M., Lü, X. Q., Zhang, J. Y., Zhao, C. Y., Tong, Y. X. & Su, C. Y. (2007). *Angew. Chem. Int. Ed.* **46**, 7399–7403.

supporting information

Acta Cryst. (2018). E74, 229-232 [https://doi.org/10.1107/S2056989018001135]

Structure of triaquatris(1,1,1-trifluoro-4-oxopentan-2-olato)cerium(III) as a possible fluorescent compound

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Computing details

Data collection: *CrystalClear* (Rigaku, 2006); cell refinement: *CrystalClear* (Rigaku, 2006); data reduction: *CrystalClear* (Rigaku, 2006) and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SIR2014* (Burla *et al.*, 2015); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Triaquatris(1,1,1-trifluoro-4-oxopentan-2-olato- κ^2O,O')cerium(III)

Crystal data

[Ce(C₅H₄F₃O₂)₃(H₂O)₃]

$M_r = 653.41$

Orthorhombic, *Pcab*

Hall symbol: -P 2bc 2ac

$a = 11.6347$ (7) Å

$b = 16.5121$ (9) Å

$c = 24.5577$ (17) Å

$V = 4717.9$ (5) Å³

$Z = 8$

$F(000) = 2552$

$D_x = 1.84$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 36866 reflections

$\theta = 3.0$ – 27.5°

$\mu = 2.04$ mm⁻¹

$T = 293$ K

Prism, yellow

$0.3 \times 0.19 \times 0.11$ mm

Data collection

Rigaku XtaLAB mini
diffractometer

Radiation source: sealed x-ray tube

Graphite monochromator

Detector resolution: 10 pixels mm⁻¹

ϕ or ω oscillation scans

Absorption correction: multi-scan
(*REQAB*; Rigaku, 1998)

$T_{\min} = 0.603$, $T_{\max} = 0.805$

45156 measured reflections

5404 independent reflections

4309 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -14 \rightarrow 15$

$k = -21 \rightarrow 21$

$l = -31 \rightarrow 31$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.092$

$S = 1.11$

5404 reflections

367 parameters

60 restraints

0 constraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 9.6633P]$

where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.78 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.44 \text{ e } \text{\AA}^{-3}$$

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ce1	0.44439 (2)	0.34074 (2)	0.44106 (2)	0.02854 (8)	
C11	0.4237 (6)	0.3197 (4)	0.2473 (2)	0.0778 (19)	
C12	0.3779 (5)	0.3321 (3)	0.30394 (19)	0.0538 (13)	
O12	0.4339 (3)	0.3049 (2)	0.34228 (12)	0.0486 (8)	
C13	0.2728 (5)	0.3716 (4)	0.3061 (2)	0.0646 (15)	
H13	0.2427	0.3924	0.2739	0.078*	
C14	0.2092 (4)	0.3819 (4)	0.3546 (2)	0.0600 (14)	
O14	0.2451 (3)	0.3617 (2)	0.40111 (12)	0.0448 (7)	
C15	0.0892 (6)	0.4173 (6)	0.3520 (3)	0.113 (3)	
H15A	0.0766	0.4406	0.3167	0.169*	
H15B	0.0812	0.4584	0.3794	0.169*	
H15C	0.0338	0.3752	0.3583	0.169*	
C21	0.4510 (5)	0.5793 (3)	0.33461 (19)	0.0586 (14)	
C22	0.5053 (4)	0.5033 (3)	0.35843 (18)	0.0439 (10)	
O22	0.4552 (3)	0.47868 (18)	0.40133 (11)	0.0408 (7)	
C23	0.5971 (5)	0.4712 (3)	0.3316 (2)	0.0536 (12)	
H23	0.6201	0.496	0.2994	0.064*	
C24	0.6600 (4)	0.4024 (3)	0.34943 (19)	0.0468 (11)	
O24	0.6358 (2)	0.36304 (19)	0.39146 (12)	0.0429 (7)	
C25	0.7622 (5)	0.3774 (4)	0.3167 (2)	0.0700 (16)	
H25A	0.7489	0.3897	0.279	0.105*	
H25B	0.7745	0.3203	0.3208	0.105*	
H25C	0.8288	0.4063	0.3292	0.105*	
C31	0.1589 (4)	0.4538 (3)	0.5562 (2)	0.0607 (14)	
C32	0.2598 (4)	0.3977 (3)	0.54542 (19)	0.0430 (10)	
O32	0.3247 (3)	0.42071 (18)	0.50708 (12)	0.0454 (7)	
C33	0.2669 (4)	0.3297 (3)	0.5767 (2)	0.0529 (12)	
H33	0.2102	0.3207	0.6027	0.063*	
C34	0.3567 (4)	0.2718 (3)	0.57165 (18)	0.0467 (11)	
O34	0.4301 (3)	0.27381 (19)	0.53500 (12)	0.0448 (7)	
C35	0.3625 (6)	0.2034 (4)	0.6122 (3)	0.0802 (19)	
H35A	0.316	0.2164	0.6433	0.12*	
H35B	0.4407	0.1958	0.6236	0.12*	
H35C	0.3346	0.1546	0.5957	0.12*	
F11B	0.4262 (11)	0.3878 (4)	0.2185 (3)	0.166 (5)	0.829 (14)
F11A	0.3683 (6)	0.2702 (5)	0.2173 (2)	0.132 (3)	0.829 (14)
F11C	0.5308 (6)	0.2914 (7)	0.2481 (2)	0.156 (5)	0.829 (14)

F11D	0.455 (3)	0.2450 (11)	0.2438 (15)	0.131 (14)*	0.171 (14)
F11E	0.503 (2)	0.3703 (15)	0.2358 (11)	0.080 (9)*	0.171 (14)
F11F	0.336 (2)	0.330 (3)	0.2134 (15)	0.149 (17)*	0.171 (14)
F21A	0.3517 (8)	0.5668 (4)	0.3129 (5)	0.148 (4)	0.838 (17)
F21B	0.5143 (11)	0.6165 (5)	0.2974 (4)	0.160 (5)	0.838 (17)
F21C	0.4371 (7)	0.6369 (2)	0.3718 (2)	0.0713 (18)	0.838 (17)
F21D	0.4696 (19)	0.5826 (17)	0.2820 (6)	0.060 (8)*	0.162 (17)
F21E	0.483 (3)	0.6448 (16)	0.3572 (13)	0.108 (15)*	0.162 (17)
F21F	0.3356 (14)	0.5734 (15)	0.3364 (10)	0.054 (7)*	0.162 (17)
F31A	0.1248 (6)	0.4523 (5)	0.6089 (2)	0.137 (3)	0.836 (11)
F31B	0.0676 (4)	0.4319 (3)	0.5295 (3)	0.110 (3)	0.836 (11)
F31C	0.1797 (4)	0.5278 (2)	0.5457 (4)	0.115 (3)	0.836 (11)
F31E	0.129 (3)	0.487 (2)	0.5071 (8)	0.125 (13)*	0.164 (11)
F31F	0.175 (4)	0.5175 (18)	0.5874 (14)	0.16 (2)*	0.164 (11)
F31D	0.065 (2)	0.419 (2)	0.5740 (17)	0.140 (16)*	0.164 (11)
O1W	0.5906 (3)	0.4133 (2)	0.50449 (13)	0.0432 (7)	
H1WA	0.627 (4)	0.455 (2)	0.495 (2)	0.065*	
H1WB	0.574 (5)	0.426 (4)	0.5364 (11)	0.065*	
O2W	0.5781 (3)	0.2200 (2)	0.45895 (15)	0.0536 (9)	
H2WA	0.629 (4)	0.193 (4)	0.442 (2)	0.08*	
H2WB	0.578 (5)	0.201 (4)	0.4904 (13)	0.08*	
O3W	0.3258 (3)	0.2079 (2)	0.44205 (16)	0.0578 (9)	
H3WA	0.270 (4)	0.186 (4)	0.425 (2)	0.087*	
H3WB	0.346 (6)	0.161 (2)	0.451 (3)	0.087*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ce1	0.02544 (11)	0.03113 (12)	0.02903 (12)	0.00204 (9)	0.00172 (9)	0.00215 (9)
C11	0.104 (6)	0.089 (5)	0.040 (3)	-0.012 (4)	-0.001 (3)	-0.008 (3)
C12	0.066 (3)	0.060 (3)	0.035 (2)	-0.015 (3)	-0.001 (2)	-0.002 (2)
O12	0.0509 (19)	0.059 (2)	0.0355 (16)	0.0012 (16)	0.0016 (14)	-0.0088 (15)
C13	0.068 (4)	0.080 (4)	0.046 (3)	0.005 (3)	-0.012 (3)	0.011 (3)
C14	0.043 (3)	0.076 (4)	0.061 (3)	0.004 (3)	-0.011 (2)	0.013 (3)
O14	0.0316 (15)	0.059 (2)	0.0437 (17)	-0.0006 (14)	-0.0022 (13)	0.0072 (14)
C15	0.066 (4)	0.174 (9)	0.097 (5)	0.054 (5)	-0.018 (4)	0.035 (6)
C21	0.089 (4)	0.046 (3)	0.041 (3)	0.010 (3)	0.004 (3)	0.011 (2)
C22	0.054 (3)	0.038 (2)	0.039 (2)	0.003 (2)	-0.003 (2)	0.0074 (18)
O22	0.0475 (17)	0.0375 (15)	0.0373 (15)	0.0058 (14)	0.0065 (13)	0.0087 (13)
C23	0.061 (3)	0.054 (3)	0.046 (3)	0.006 (2)	0.015 (2)	0.019 (2)
C24	0.036 (2)	0.060 (3)	0.044 (2)	0.004 (2)	0.008 (2)	0.011 (2)
O24	0.0314 (15)	0.0551 (18)	0.0423 (17)	0.0061 (13)	0.0063 (13)	0.0154 (14)
C25	0.055 (3)	0.093 (4)	0.062 (3)	0.014 (3)	0.027 (3)	0.014 (3)
C31	0.040 (3)	0.057 (3)	0.085 (4)	0.000 (2)	0.014 (3)	-0.019 (3)
C32	0.030 (2)	0.049 (3)	0.049 (3)	-0.0027 (19)	0.0042 (19)	-0.016 (2)
O32	0.0467 (17)	0.0472 (17)	0.0424 (16)	0.0084 (15)	0.0108 (14)	-0.0012 (14)
C33	0.046 (3)	0.061 (3)	0.051 (3)	-0.004 (2)	0.021 (2)	-0.001 (2)
C34	0.047 (3)	0.054 (3)	0.039 (2)	-0.008 (2)	0.007 (2)	0.002 (2)

O34	0.0467 (18)	0.0533 (19)	0.0343 (15)	0.0073 (15)	0.0087 (14)	0.0063 (14)
C35	0.095 (5)	0.078 (4)	0.068 (4)	0.007 (4)	0.030 (3)	0.032 (3)
F11B	0.274 (13)	0.152 (7)	0.073 (4)	0.019 (7)	0.064 (6)	0.042 (4)
F11A	0.142 (6)	0.173 (7)	0.082 (4)	-0.010 (5)	-0.013 (4)	-0.076 (4)
F11C	0.099 (5)	0.305 (13)	0.065 (3)	0.041 (7)	0.018 (3)	-0.036 (5)
F21A	0.196 (8)	0.097 (4)	0.151 (7)	0.052 (5)	-0.128 (6)	-0.018 (5)
F21B	0.238 (10)	0.096 (5)	0.146 (7)	0.068 (6)	0.108 (7)	0.087 (5)
F21C	0.105 (5)	0.040 (2)	0.069 (3)	0.012 (2)	-0.006 (3)	0.0032 (19)
F31A	0.129 (6)	0.175 (7)	0.106 (5)	0.071 (5)	0.053 (4)	-0.015 (4)
F31B	0.049 (3)	0.090 (4)	0.191 (7)	0.017 (2)	-0.034 (3)	-0.047 (4)
F31C	0.075 (3)	0.042 (2)	0.228 (9)	0.005 (2)	0.055 (4)	-0.021 (3)
O1W	0.0436 (17)	0.0465 (18)	0.0396 (17)	-0.0101 (14)	-0.0018 (14)	-0.0037 (15)
O2W	0.048 (2)	0.059 (2)	0.054 (2)	0.0261 (16)	0.0161 (16)	0.0169 (17)
O3W	0.059 (2)	0.0420 (18)	0.072 (2)	-0.0178 (17)	-0.0242 (19)	0.0094 (17)

Geometric parameters (Å, °)

Ce1—O22	2.481 (3)	C22—O22	1.271 (5)
Ce1—O12	2.500 (3)	C22—C23	1.362 (7)
Ce1—O32	2.512 (3)	C23—C24	1.420 (7)
Ce1—O14	2.542 (3)	C23—H23	0.93
Ce1—O34	2.563 (3)	C24—O24	1.252 (5)
Ce1—O24	2.565 (3)	C24—C25	1.493 (6)
Ce1—O2W	2.566 (3)	C25—H25A	0.96
Ce1—O3W	2.592 (3)	C25—H25B	0.96
Ce1—O1W	2.599 (3)	C25—H25C	0.96
C11—F11A	1.276 (7)	C31—F31C	1.273 (7)
C11—F11E	1.280 (15)	C31—F31B	1.299 (6)
C11—F11D	1.289 (16)	C31—F31D	1.308 (17)
C11—F11B	1.328 (8)	C31—F31F	1.315 (17)
C11—F11F	1.330 (16)	C31—F31A	1.354 (7)
C11—F11C	1.331 (8)	C31—F31E	1.372 (16)
C11—C12	1.504 (8)	C31—C32	1.518 (6)
C12—O12	1.230 (6)	C32—O32	1.266 (5)
C12—C13	1.387 (8)	C32—C33	1.365 (7)
C13—C14	1.413 (8)	C33—C34	1.422 (7)
C13—H13	0.93	C33—H33	0.93
C14—O14	1.262 (6)	C34—O34	1.241 (5)
C14—C15	1.514 (8)	C34—C35	1.507 (7)
C15—H15A	0.96	C35—H35A	0.96
C15—H15B	0.96	C35—H35B	0.96
C15—H15C	0.96	C35—H35C	0.96
C21—F21E	1.273 (15)	O1W—H1WA	0.84 (2)
C21—F21A	1.289 (8)	O1W—H1WB	0.83 (2)
C21—F21D	1.312 (14)	O2W—H2WA	0.85 (2)
C21—F21B	1.324 (7)	O2W—H2WB	0.84 (2)
C21—F21C	1.329 (6)	O3W—H3WA	0.85 (2)
C21—F21F	1.347 (15)	O3W—H3WB	0.84 (2)

C21—C22	1.522 (6)		
O22—Ce1—O12	80.70 (11)	F21A—C21—F21B	106.6 (7)
O22—Ce1—O32	78.42 (10)	F21A—C21—F21C	106.8 (6)
O12—Ce1—O32	136.35 (11)	F21B—C21—F21C	102.1 (6)
O22—Ce1—O14	76.68 (10)	F21E—C21—F21F	109.9 (15)
O12—Ce1—O14	67.23 (10)	F21D—C21—F21F	101.5 (12)
O32—Ce1—O14	70.85 (10)	F21E—C21—C22	114.3 (17)
O22—Ce1—O34	138.85 (10)	F21A—C21—C22	113.6 (5)
O12—Ce1—O34	140.17 (11)	F21D—C21—C22	110.2 (13)
O32—Ce1—O34	67.04 (10)	F21B—C21—C22	114.7 (5)
O14—Ce1—O34	110.31 (10)	F21C—C21—C22	112.1 (4)
O22—Ce1—O24	68.74 (10)	F21F—C21—C22	110.0 (12)
O12—Ce1—O24	67.40 (10)	O22—C22—C23	129.5 (4)
O32—Ce1—O24	135.42 (10)	O22—C22—C21	113.1 (4)
O14—Ce1—O24	126.11 (10)	C23—C22—C21	117.4 (4)
O34—Ce1—O24	123.05 (9)	C22—O22—Ce1	130.0 (3)
O22—Ce1—O2W	138.56 (11)	C22—C23—C24	124.5 (4)
O12—Ce1—O2W	90.68 (12)	C22—C23—H23	117.7
O32—Ce1—O2W	129.33 (11)	C24—C23—H23	117.7
O14—Ce1—O2W	136.45 (12)	O24—C24—C23	123.6 (4)
O34—Ce1—O2W	63.28 (10)	O24—C24—C25	118.7 (4)
O24—Ce1—O2W	70.52 (10)	C23—C24—C25	117.7 (4)
O22—Ce1—O3W	143.87 (11)	C24—O24—Ce1	131.4 (3)
O12—Ce1—O3W	77.44 (12)	C24—C25—H25A	109.5
O32—Ce1—O3W	98.26 (12)	C24—C25—H25B	109.5
O14—Ce1—O3W	68.46 (11)	H25A—C25—H25B	109.5
O34—Ce1—O3W	65.93 (11)	C24—C25—H25C	109.5
O24—Ce1—O3W	126.04 (12)	H25A—C25—H25C	109.5
O2W—Ce1—O3W	70.35 (13)	H25B—C25—H25C	109.5
O22—Ce1—O1W	77.26 (10)	F31C—C31—F31B	108.7 (6)
O12—Ce1—O1W	136.27 (11)	F31D—C31—F31F	105.9 (17)
O32—Ce1—O1W	74.57 (11)	F31C—C31—F31A	105.5 (5)
O14—Ce1—O1W	139.99 (11)	F31B—C31—F31A	103.7 (6)
O34—Ce1—O1W	72.65 (10)	F31D—C31—F31E	105.0 (16)
O24—Ce1—O1W	69.51 (10)	F31F—C31—F31E	103.0 (16)
O2W—Ce1—O1W	81.87 (12)	F31C—C31—C32	113.8 (4)
O3W—Ce1—O1W	137.14 (11)	F31B—C31—C32	112.0 (4)
F11E—C11—F11D	113.8 (16)	F31D—C31—C32	115.9 (17)
F11A—C11—F11B	104.2 (7)	F31F—C31—C32	118.7 (19)
F11E—C11—F11F	109.5 (15)	F31A—C31—C32	112.5 (5)
F11D—C11—F11F	107.7 (16)	F31E—C31—C32	106.8 (14)
F11A—C11—F11C	104.9 (7)	O32—C32—C33	129.0 (4)
F11B—C11—F11C	106.6 (8)	O32—C32—C31	114.2 (4)
F11A—C11—C12	116.3 (6)	C33—C32—C31	116.8 (4)
F11E—C11—C12	111.8 (13)	C32—O32—Ce1	130.8 (3)
F11D—C11—C12	106.9 (17)	C32—C33—C34	123.3 (4)
F11B—C11—C12	112.7 (6)	C32—C33—H33	118.4

F11F—C11—C12	106.7 (19)	C34—C33—H33	118.4
F11C—C11—C12	111.4 (5)	O34—C34—C33	123.5 (4)
O12—C12—C13	127.6 (5)	O34—C34—C35	117.9 (5)
O12—C12—C11	118.1 (5)	C33—C34—C35	118.6 (4)
C13—C12—C11	114.3 (5)	C34—O34—Ce1	135.1 (3)
C12—O12—Ce1	133.0 (3)	C34—C35—H35A	109.5
C12—C13—C14	123.4 (5)	C34—C35—H35B	109.5
C12—C13—H13	118.3	H35A—C35—H35B	109.5
C14—C13—H13	118.3	C34—C35—H35C	109.5
O14—C14—C13	123.9 (5)	H35A—C35—H35C	109.5
O14—C14—C15	116.4 (5)	H35B—C35—H35C	109.5
C13—C14—C15	119.6 (5)	Ce1—O1W—H1WA	123 (4)
C14—O14—Ce1	133.5 (3)	Ce1—O1W—H1WB	122 (4)
C14—C15—H15A	109.5	H1WA—O1W—H1WB	100 (5)
C14—C15—H15B	109.5	Ce1—O2W—H2WA	138 (4)
H15A—C15—H15B	109.5	Ce1—O2W—H2WB	117 (4)
C14—C15—H15C	109.5	H2WA—O2W—H2WB	105 (6)
H15A—C15—H15C	109.5	Ce1—O3W—H3WA	140 (5)
H15B—C15—H15C	109.5	Ce1—O3W—H3WB	129 (5)
F21E—C21—F21D	110.2 (15)	H3WA—O3W—H3WB	87 (6)
F11A_a—C11—C12—O12	109.7 (8)	F21C—C21—C22—C23	-130.5 (6)
F11E—C11—C12—O12	-79.3 (17)	F21F—C21—C22—C23	137.2 (12)
F11D—C11—C12—O12	45.9 (19)	C23—C22—O22—Ce1	-24.8 (8)
F11B—C11—C12—O12	-130.0 (8)	C21—C22—O22—Ce1	154.3 (3)
F11F—C11—C12—O12	161.0 (19)	O22—C22—C23—C24	-3.3 (9)
F11C—C11—C12—O12	-10.3 (9)	C21—C22—C23—C24	177.6 (5)
F11A—C11—C12—C13	-68.2 (9)	C22—C23—C24—O24	1.5 (9)
F11E—C11—C12—C13	102.7 (16)	C22—C23—C24—C25	-177.0 (5)
F11D—C11—C12—C13	-132.0 (19)	C23—C24—O24—Ce1	27.8 (7)
F11B—C11—C12—C13	52.0 (10)	C25—C24—O24—Ce1	-153.7 (4)
F11F—C11—C12—C13	-17.0 (19)	F31C—C31—C32—O32	-30.8 (8)
F11C—C11—C12—C13	171.7 (8)	F31B—C31—C32—O32	92.9 (7)
C13—C12—O12—Ce1	-25.9 (8)	F31D—C31—C32—O32	148 (2)
C11—C12—O12—Ce1	156.4 (4)	F31F—C31—C32—O32	-84 (2)
O12—C12—C13—C14	-4.5 (10)	F31A—C31—C32—O32	-150.7 (6)
C11—C12—C13—C14	173.2 (6)	F31E—C31—C32—O32	31.9 (18)
C12—C13—C14—O14	5.5 (10)	F31C—C31—C32—C33	150.7 (6)
C12—C13—C14—C15	-173.0 (7)	F31B—C31—C32—C33	-85.6 (7)
C13—C14—O14—Ce1	23.3 (9)	F31D—C31—C32—C33	-30 (2)
C15—C14—O14—Ce1	-158.2 (5)	F31F—C31—C32—C33	98 (2)
F21E—C21—C22—O22	82.1 (19)	F31A—C31—C32—C33	30.8 (7)
F21A—C21—C22—O22	-70.9 (8)	F31E—C31—C32—C33	-146.6 (17)
F21D—C21—C22—O22	-153.2 (11)	C33—C32—O32—Ce1	28.9 (7)
F21B—C21—C22—O22	166.1 (9)	C31—C32—O32—Ce1	-149.4 (3)
F21C—C21—C22—O22	50.2 (7)	O32—C32—C33—C34	2.2 (8)
F21F—C21—C22—O22	-42.1 (12)	C31—C32—C33—C34	-179.6 (5)
F21E—C21—C22—C23	-98.6 (19)	C32—C33—C34—O34	-7.2 (8)

F21A—C21—C22—C23	108.4 (9)	C32—C33—C34—C35	173.8 (5)
F21D—C21—C22—C23	26.1 (13)	C33—C34—O34—Ce1	-19.7 (7)
F21B—C21—C22—C23	-14.6 (11)	C35—C34—O34—Ce1	159.3 (4)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1 <i>W</i> —H1 <i>WA</i> ...O32 ⁱ	0.84 (2)	2.13 (3)	2.927 (4)	158 (5)
O1 <i>W</i> —H1 <i>WB</i> ...O22 ⁱ	0.83 (2)	2.23 (4)	2.969 (4)	149 (6)
O2 <i>W</i> —H2 <i>WA</i> ...O14 ⁱⁱ	0.85 (2)	1.91 (2)	2.759 (4)	177 (6)
O3 <i>W</i> —H3 <i>WA</i> ...O24 ⁱⁱⁱ	0.85 (2)	1.94 (2)	2.792 (4)	176 (7)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1/2, -y+1/2, z$; (iii) $x-1/2, -y+1/2, z$.