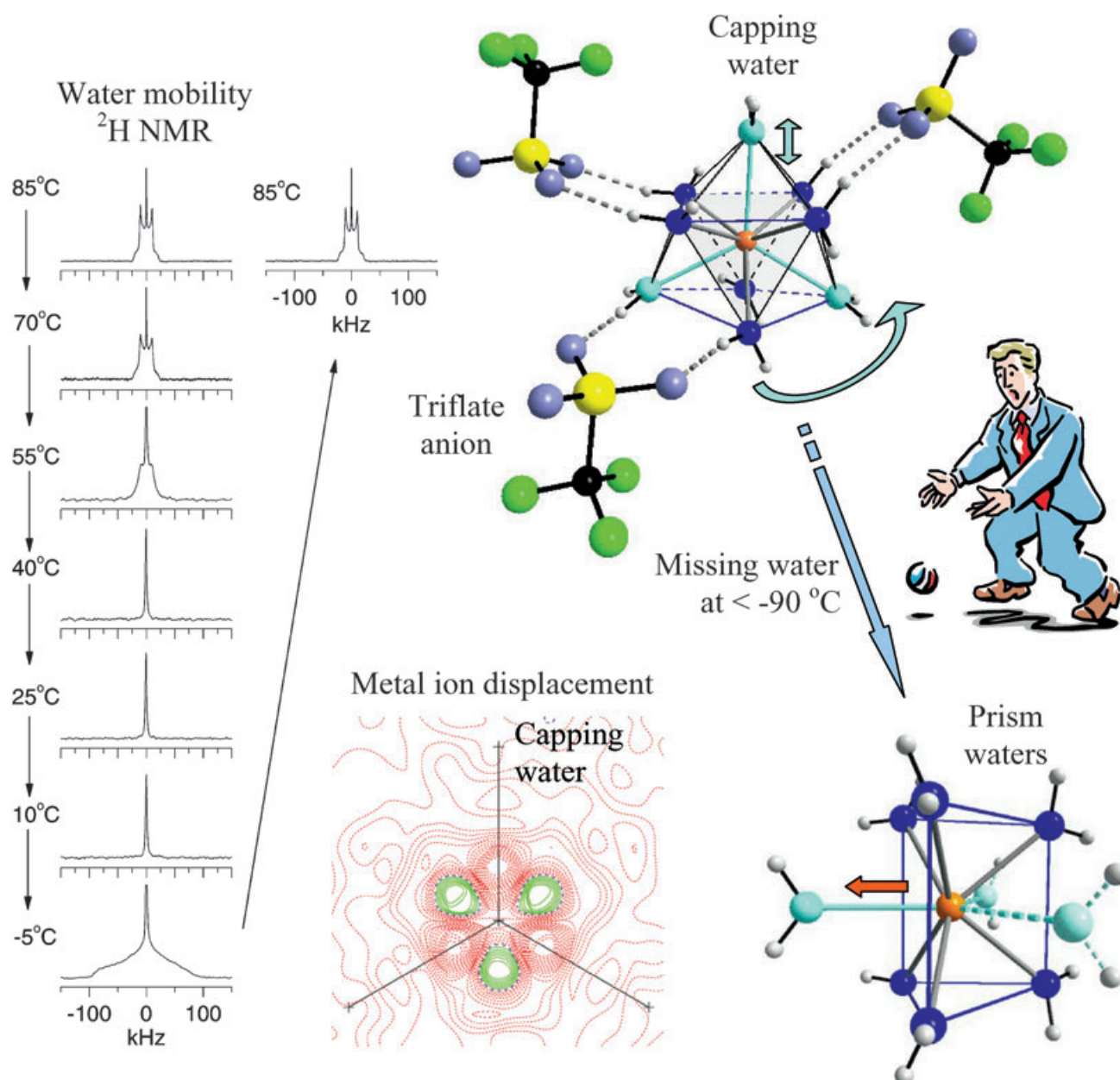


## Trivalent metal ion hydrates with mobile and missing water, stabilised by hydrogen bonding



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# Highly Hydrated Cations: Deficiency, Mobility, and Coordination of Water in Crystalline Nonahydrated Scandium(III), Yttrium(III), and Lanthanoid(III) Trifluoromethanesulfonates

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**Abstract:** Trivalent lanthanide-like metal ions coordinate nine water oxygen atoms, which form a tricapped trigonal prism in a large number of crystalline hydrates. Water deficiency, randomly distributed over the capping positions, was found for the smallest metal ions in the isomorphous nonahydrated trifluoromethanesulfonates,  $[M(H_2O)_n](CF_3SO_3)_3$ , in which  $M = Sc^{III}$ ,  $Lu^{III}$ ,  $Yb^{III}$ ,  $Tm^{III}$  or  $Er^{III}$ . The hydration number  $n$  increases ( $n = 8.0(1)$ ,  $8.4(1)$ ,  $8.7(1)$ ,  $8.8(1)$  and  $8.96(5)$ , respectively) with increasing ionic size. Deuterium ( $^2H$ ) solid-state NMR spectroscopy revealed fast positional exchange between the coordinated capping and prism water molecules; this exchange started at temperatures higher than

about 280 K for lutetium(III) and below 268 K for scandium(III). Similar positional exchange for the fully nonahydrated yttrium(III) and lanthanum(III) compounds started at higher temperatures, over about 330 and 360 K, respectively. An exchange mechanism is proposed that can exchange equatorial and capping water molecules within the restrictions of the crystal lattice, even for fully hydrated lanthanoid(III) ions. Phase transitions occurred for all the water-deficient compounds at  $\approx 185$  K. The hydrated scandium(III)

trifluoromethanesulfonate transforms reversibly ( $\Delta H^\circ = -0.80(1)$  kJ mol<sup>-1</sup> on cooling) to a trigonal unit cell that is almost nine times larger, with the scandium ion surrounded by seven fully occupied and two partly occupied oxygen atom positions in a distorted capped trigonal prism. The hydrogen bonding to the trifluoromethanesulfonate anions stabilises the trigonal prism of water ligands, even for the crowded hydration sphere of the smallest metal ions in the series. Implications for the Lewis acid catalytic activity of the hydrated scandium(III) and lanthanoid(III) trifluoromethanesulfonates for organic syntheses performed in aqueous media are discussed.

**Keywords:** hydrates • hydrogen bonds • lanthanoids • scandium • structure elucidation

## Introduction

The coordination geometry, the hydration number and the water-exchange reactions of metal ions in solution are of primary importance in interpreting the thermodynamic and kinetic properties. For solutions, investigations of the structure and dynamic behaviour must often rely on comparisons with three-dimensional information from crystal structures and computer simulations.<sup>[1]</sup> However, when compounds with strongly hydrated metal ions crystallise from saturated solutions even anions regarded as noncoordinating are frequently found attached to the metal ion. Striking examples of such anion effects on the hydrated metal ion are found for the isoelectronic mercury(II) and thallium(III) ions, which are hexahydrated in solution and in their perchlorate salts but which crystallise from trifluoromethanesulfonate solutions with lower hydration numbers in the compounds bis-

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aquamercury(II) trifluoromethanesulfonate,  $[\text{Hg}(\text{OH}_2)_2(\text{CF}_3\text{SO}_3)_2]_{\text{aq}}$ , and tris(aqua)thallium(III) trifluoromethanesulfonate,  $[\text{Tl}(\text{OH}_2)_3(\text{CF}_3\text{SO}_3)_3]$ , respectively.<sup>[2-5]</sup>

The lanthanoid(III) ions, La<sup>III</sup> to Lu<sup>III</sup>, have surprisingly been proposed to form hexahydrated perchlorates, isostructural to the hexa(aqua)thallium(III) perchlorate.<sup>[5]</sup> However, from trifluoromethanesulfonate solutions they crystallise with higher hydration numbers in a series of nonhydrated trifluoromethanesulfonate salts, as do the isostructural Group 3 metal ions, scandium(III), yttrium(III) and lanthanum(III).<sup>[6-8]</sup> The isomorphous series of nonaqua lanthanoid(III) ethylsulfates belongs to the same space group  $P6_3/m$ ,<sup>[9-11]</sup> in which the metal ions are located in a crystallographic site that is surrounded by six equidistant water molecules in a trigonal prism with the rectangular sides capped by three more-distant water molecules.

The rapidly growing technological importance for catalysis, liquid–liquid extraction, organic synthesis, etc. of the trivalent ions of Group 3, scandium, yttrium and lanthanum, as well as the series of lanthanoid(III) ions, has stimulated experimental and theoretical activity that aims to explain the basic properties.<sup>[12,13]</sup> The series of lanthanoid(III) ions, in which the size decreases with increasing atomic number,<sup>[14]</sup> provides unique possibilities for experimentally testing and verifying theoretical models of coordination and bonding. For example, while the size decreases the difference between the two groups of Ln<sup>III</sup>–O distances in the tricapped trigonal prism (TTP) increases from lanthanum (atomic no. 57) to lutetium (atomic no. 71).<sup>[15]</sup>

The currently favoured description of the primary hydration number of the lanthanoid(III) ions in solution interprets trends in physical properties of the aqueous solutions, for example, partial molar volumes or water exchange rates, by assuming a distinct change in the hydration number from nine to eight somewhere in the middle of the series.<sup>[1]</sup> For example, results from molecular dynamics (MD) simulations have been used to describe a structural transition at the samarium(III) ion in aqueous solution.<sup>[16]</sup> However, the same MD studies also showed that the proposed transition from the TTP to square antiprismatic configuration critically depends on the type of force field used to describe the coordinated water molecules, particularly that used for the hydrogen bonding.

This view of an abrupt transition in the hydration polygon has been questioned, and similar experimental results have been interpreted without such an assumption.<sup>[17]</sup> Also, a recent MD simulation of dilute aqueous solutions of neodymium(III), gadolinium(III) and ytterbium(III) ions by Floris and Tani, with *ab initio* effective pair potentials within a polarisable continuum, favours the TTP configuration for all three aqua ions, even though more frequent distortions appear for the smallest of those ions, ytterbium(III).<sup>[18]</sup>

The mean M<sup>III</sup>–O distance from crystal structures of the trifluoromethanesulfonate salts of the hydrated d<sup>0</sup> ions of Group 3 (2.55, 2.40 and 2.28 Å for M = La, Y and Sc, respectively) changes substantially for nine coordination in the

TTP configuration.<sup>[10,19,20]</sup> However, in aqueous solution only the largest ion, lanthanum(III), coordinates nine water molecules;<sup>[21]</sup> the yttrium(III) ion coordinates eight,<sup>[19]</sup> while the hydration number of the relatively small scandium(III) ion is probably around seven,<sup>[1]</sup> with the mean M–O distances being 2.54–2.58,<sup>[21]</sup> 2.37<sup>[19]</sup> and 2.17–2.18 Å,<sup>[22,23]</sup> respectively, in asymmetric radial distributions.

To investigate the reason for the high stability of the TTP configuration in crystal structures, which is evident even for some rather small trivalent ions with very crowded hydration spheres, we compared structural relationships, including hydrogen bonding and anion effects, for the hydrated trivalent Group 3 and lanthanoid(III) metal ions in isostructural crystalline hydrates. The combination of temperature-dependent crystallography and <sup>2</sup>H solid-state NMR spectroscopy information in the present study revealed unexpected results concerning deficiency and positional exchange of the coordinated water for the highly hydrated trifluoromethanesulfonate compounds. Further work is in progress, and we have recently performed vibrational and extended X-ray absorption fine-structure (EXAFS) spectroscopy studies of the M–O coordination and bonding in a series of lanthanoid(III) ions solvated with several oxygen-donor solvents, both in solution and in the solid state.<sup>[24,25]</sup> The trends we observe do not support the previously proposed abrupt structural transition in the series of lanthanoid(III) aqua ions in aqueous solution,<sup>[1]</sup> and we will discuss the structures in solution in a forthcoming paper.

Scandium(III) and lanthanoid(III) trifluoromethanesulfonates are efficient and water-tolerant Lewis acid catalysts, which allow many organic syntheses to be performed, even in aqueous media.<sup>[12,13]</sup> The reason why the solvated scandium(III) trifluoromethanesulfonate often shows the highest catalytic activity was another point of interest for the structure studies.

## Results and Discussion

**Water deficiency in crystal structures:** X-ray diffraction data were collected at ambient temperature for the hydrated trifluoromethanesulfonates  $[\text{M}(\text{H}_2\text{O})_n](\text{CF}_3\text{SO}_3)_3$ , in which M = Sc (**1**), Lu (**2**), Yb (**3**), Tm (**4**), Er (**5**) or Tb (**6**), and the parameters of the crystal structures were refined. The trivalent metal ions are located in the (2c) site of  $\bar{6}$  symmetry of the space group  $P6_3/m$ . Six surrounding water oxygen atoms ( $\text{O}_p$ ) are located at the vertices of a trigonal prism, with three capping water oxygen atoms ( $\text{O}_c$ ) slightly displaced from the centre of the rectangular surfaces. The crystallographically determined positions correspond to two groups of M–O bond lengths, 6M– $\text{O}_p$  and 3M– $\text{O}_c$  (Table 1). All water molecules form single hydrogen bonds to oxygen atoms of trifluoromethanesulfonate ions (Figure 1). The structures of the isomorphous yttrium(III) and lanthanoid(III) compounds,  $[\text{M}(\text{H}_2\text{O})_9](\text{CF}_3\text{SO}_3)_3$  (M = Y and La to Lu, except Tm, Er and Pm), have been discussed in detail elsewhere.<sup>[6,7]</sup>

Table 1. Metal–oxygen bond lengths in the tricapped trigonal prism, hydrogen-bond lengths from water molecules to trifluoromethanesulfonate ions and closest oxygen–oxygen contact distances.<sup>[a]</sup>

	M–O <sub>p</sub>	M–O <sub>c</sub>	O <sub>p</sub> –H···O <sub>t</sub>	O <sub>c</sub> –H···O <sub>t</sub>	O <sub>p</sub> ···O <sub>p</sub> <sup>[d]</sup> , O <sub>p</sub> ···O <sub>p</sub> <sup>[e]</sup>	O <sub>c</sub> ···O <sub>p</sub>
Sc <sup>[b]</sup> (1)	2.169(3)	2.439(6)	2.781(4), 2.796(4)	2 × 2.989(4)	2 × 2.748(4), 2.959(6)	2 × 2.561(6), 2 × 2.649(6)
Lu <sup>[b]</sup> (2)	2.287(4)	2.499(8)	2.734(6), 2.796(6)	2 × 2.993(6)	2 × 2.846(7), 3.182(9)	2 × 2.641(8), 2 × 2.788(8)
Yb <sup>[b]</sup> (3)	2.304(2)	2.523(4)	2.756(3), 2.802(3)	2 × 3.011(3)	2 × 2.842(4), 3.234(5)	2 × 2.663(4), 2 × 2.827(4)
Tm <sup>[b]</sup> (4)	2.322(3)	2.522(5)	2.745(4), 2.812(4)	2 × 3.006(3)	2 × 2.844(6), 3.283(6)	2 × 2.663(5), 2 × 2.855(5)
Er <sup>[b]</sup> (5)	2.340(2)	2.518(4)	2.740(4), 2.814(4)	2 × 2.999(3)	2 × 2.865(4), 3.309(5)	2 × 2.677(4), 2 × 2.855(4)
Y <sup>[c]</sup>	2.344(3)	2.525(6)	2.750(6), 2.830(3)	2 × 3.004(5)	2 × 2.862(4), 3.324(5)	2 × 2.688(4), 2 × 2.861(6)
Tb <sup>[b]</sup> (6)	2.383(2)	2.530(3)	2.749(3), 2.829(3)	2 × 2.979(3)	2 × 2.904(3), 3.387(4)	2 × 2.699(3), 2 × 2.901(3)
La <sup>[c]</sup>	2.519(2)	2.619(5)	2.755(5), 2.840(2)	2 × 2.932(4)	2 × 3.082(4), 3.551(3)	2 × 2.793(3), 2 × 3.041(5)

[a] Oxygen atoms: p = prism, c = capping, t = trifluoromethanesulfonate. [b] Results from this work. [c] Results from ref. [6]. [d] Side of triangular surface. [e] Side of rectangular surface of the trigonal prism.

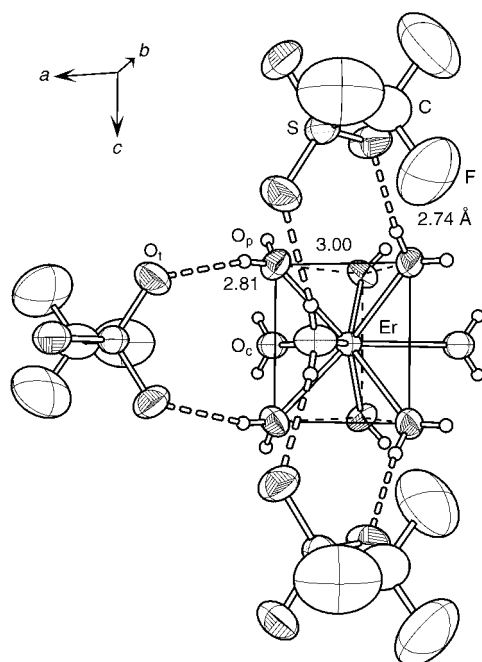


Figure 1. The trigonal prism (O<sub>p</sub>) and capping (O<sub>c</sub>) water oxygen atoms around the nonhydrated erbium(III) ion and the bridging hydrogen bonds (O···O distances given in Å) formed to the oxygen atoms (O<sub>t</sub>) of the trifluoromethanesulfonate ions, displayed with 50% probability ellipsoids for non-hydrogen atoms.

The analyses (Table 2) showed that the water/metal molar ratio increases from about 8.0 up to 9.0 for the crystalline compounds 1–6. Refinement of the site-occupancy factors in all cases resulted in full occupancy of the prism positions, with 6.0 O<sub>p</sub> atoms, while occupancy numbers of 0.67(1),

Table 2. The average number of water molecules, *n*, in the TTP hydrates [M(H<sub>2</sub>O)<sub>*n*</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> from the X-ray diffraction site-occupancy factors, TGA analysis and crystal density.

M	XRD	TGA	Density
Sc (1)	8.02(4)	8.1(1)	8.0(1)
Lu (2)	8.46(9)	8.4(1)	8.4(1)
Yb (3)	8.72(3)	— <sup>[a]</sup>	8.7(1)
Tm (4)	8.84(5)	— <sup>[a]</sup>	8.7(1)
Er (5)	8.96(5)	— <sup>[a]</sup>	8.8(1)
Tb (6)	9.00	— <sup>[a]</sup>	9.0(1)

[a] Further decomposition prevented accurate analysis. See Figure S2 in the Supporting Information.

0.82(3), 0.91(1), 0.945(14) and 0.988(17) were obtained for the three capping (O<sub>c</sub>) positions of the scandium(III), lutetium(III), ytterbium(III), thulium(III) and erbium(III) TTP hydrates, respectively. The occupancy factor obtained from refinements on data collected for ytterbium(III) crystals at different occasions varied from 0.87 to 0.95. The numbers obtained were somewhat correlated to the weighting of the data sets but could also reflect some variation in the water content for different preparations.

**Residual electron-density maps:** The refined occupancy factors for the crystal structures located the water deficiency to the capping positions of the scandium(III), lutetium(III), ytterbium(III), thulium(III) and erbium(III) TTP hydrates (1–5). The site symmetry  $\bar{6}$  imposed by the space group *P6<sub>3</sub>/m* on the metal ions requires a random distribution of the vacancies. The *U*<sub>11</sub> component of the thermal ellipsoid in the plane of the capping waters is abnormally high for the metal ions in the water-deficient compounds 1–5, with the highest value occurring with scandium, while the perpendicular *U*<sub>33</sub> component on average shows the slight decrease expected for decreasing ionic radii (Figure 2). The *U*<sub>11</sub> value of scandium remains high even at lower temperatures (293, 250 and 200 K), a fact revealing positional disorder of the metal atoms in the equatorial plane containing the capping oxygen atoms, rather than high thermal motion. A difference electron-density map of this region illustrates the disorder (Figure 3). Three domains of electron deficiency occur along the Sc–O<sub>c</sub> bond directions, with three intermediate regions of excess electron density. The three maxima, symmetrically located about 0.7 Å from the crystallographic position (1/3, 2/3, 1/4) of scandium, correspond to the expected directions of displacement of the scandium atom induced by an opposite empty capping (O<sub>c</sub>) position. Similar successively less pronounced electron density features are also observed around the lutetium, ytterbium, thulium and erbium ions, but these features are absent for the fully hydrated terbium ion (Figure 3). Such a pattern in the difference electron-density map has previously been observed for the two smallest lanthanoid ions, lutetium(III) and ytterbium(III), in a study of a series of [M(H<sub>2</sub>O)<sub>9</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> compounds, and it was then proposed to be a 4f–5d contribution to the electron density.<sup>[7]</sup> However, for scandium(III), without f or d electrons, the residual electron density in the high-symmetry space group

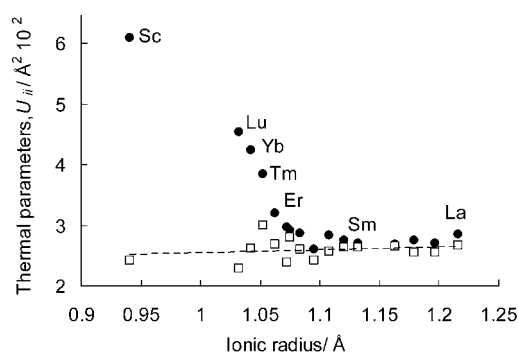


Figure 2. Anisotropic displacement parameters for the  $M^{III}$  ion (ionic radius given in Å for nine coordination) in the TTP hydrates,  $[M(H_2O)_n](CF_3SO_3)_3$ , at room temperature for  $M = Sc$  (0.925), Lu (1.032), Yb (1.042), Tm (1.052), Er (1.062), Ho (1.072), Dy (1.083), Tb (1.095), Gd (1.107), Eu (1.120), Sm (1.132), Nd (1.163), Pr (1.179), Ce (1.196), Y (1.075) and La (1.216).  $U_{11}$  (●) is the equatorial thermal ellipsoid component, with the  $U_{33}$  component (□) being perpendicular to the plane of the capping waters (see refs. [6,7] and Table S1 in the Supporting Information). The dashed line displays the slight increase in the  $U_{33}$  values expected for increasing ionic radii. For water-deficient compounds, positional disorder of the metal atom in the equatorial plane induces an abnormally large  $U_{11}$  value.

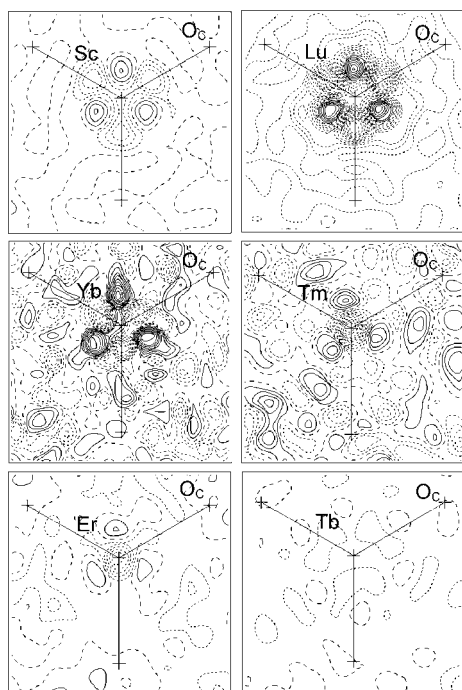


Figure 3. Residual electron density in the plane of the capping oxygen atoms ( $O_c$ ) for  $[M(H_2O)_n](CF_3SO_3)_3$  in which  $M = Sc, Lu, Yb, Tm, Er$  or  $Tb$ , with positive (solid line) and negative (dotted line) contours (interval = 0.20 Å). Min, max values ( $e \text{ Å}^{-3}$ ): Sc -0.60, 1.00; Lu -3.20, 1.40; Yb -1.60, 1.80; Tm -2.40, 1.20; Er -1.00, 1.00; Tb -0.40, 1.00. Water deficiency in  $O_c$  positions ( $n < 9$ ) displaces the metal ion.

$P6_3/m$  is clearly a disorder effect, and this is certainly also the case for all the water-deficient  $[M(H_2O)_n](CF_3SO_3)_3$  hydrates ( $M = Sc, Lu, Yb, Tm$  or  $Er$ ).

We recorded EXAFS spectra of the metal ions in these water-deficient solid hydrates and modelled the data with

two groups of  $M-O$  bond lengths.<sup>[25]</sup> The displacement of the metal ion resulting in asymmetric distributions of the distances in the two groups requires careful EXAFS data evaluation. Our preliminary results show a mean value of the first group closely similar to the crystallographic  $M-O_p$  distance, but for the second group the EXAFS mean value is somewhat shorter, up to 0.1 Å, than the crystallographic  $M-O_c$  distance. The shorter average  $M-O_c$  value probably reflects the displacement of the metal atoms in sites with water deficiency towards the two remaining capping waters, while the closest  $M-O_p$  bond lengths to the prism water oxygen atoms change less. This is consistent with difference electron-density maps in the plane through the metal and two  $O_p$  atoms for the scandium(III) structure **1** (Figure S1 in the Supporting Information), in which excess electron density both at the metal and the  $O_p$  positions indicates a correlated displacement of the metal and the  $O_p$  atoms. The thermal parameters of the  $O_p$  atoms increase with increasing water deficiency, compared, for example, to the fully hydrated terbium compound **6** (see Table S1 in the Supporting Information). Thus, some distances given in Table 1, which are based on crystallographically averaged values for the atom sites, will deviate from the true interatomic distances, especially for the highly water-deficient scandium(III) compound **1**.

The most favourable polyhedron formed by minimising the total repulsion energy for nine equidistant ligand atoms around a central metal ion is a tricapped trigonal prism.<sup>[26]</sup> Compressing the trigonal prism along the threefold axis decreases all four ligand–ligand distances for each capping atom, but two ligand–ligand distances increase and two decrease for each prism atom. Hence, each  $O_c$  capping oxygen atom in a TTP hydrate will experience greater repulsion from its oxygen neighbours than each  $O_p$  prism atom, a fact resulting in a longer  $M-O_c$  distance and a decreasing difference between the  $M-O_c$  and  $M-O_p$  distances with increasing ionic size (see Table 1). For six coordination, the  $M-O_p$  distances in a trigonal prism generally become longer than the  $M-O$  distances in an octahedral configuration, because of the shorter  $O_p \cdots O_p$  distances. Thus, oxygen atoms capping the rectangular surfaces, which approach the highly charged central ion rather closely, are required to stabilise the trigonal prism configuration from an electrostatic point of view.

**Scandium(III) hydration:** Conflicting results have been reported for the scandium(III) hydration in aqueous solution, and the hydration numbers for scandium(III) aqua ions reported for crystal structures also span an unexpectedly large range of 6–9. Several computational studies have been performed on the isolated “gas-phase” hydrates of scandium(III) with the aim of providing a better understanding of the hydration structure, the water exchange rate and the mechanisms in aqueous solution.<sup>[27–29]</sup> Åkesson et al. found the heptahydrated scandium(III) ion (in  $C_2$  symmetry) to be more stable than the hexahydrated ion ( $T_h$ ),<sup>[27]</sup> while Rotzinger proposed that hexa- and heptahydrated ions may coexist in aqueous solution.<sup>[28]</sup> Rudolph and Pye claimed that

the hexaaquascandium(III) ion, for which they calculated a surprisingly long Sc–O bond length of 2.18 Å, would be the most stable, also in aqueous solution.<sup>[29]</sup>

For structural studies of aqua ions in solution, the mean metal–oxygen bond length is often a more reliable indicator of the coordination number than direct determinations of the number of coordinated ligands.<sup>[30]</sup> The hydration number for the yttrium(III) ion in aqueous solution could be determined by comparing X-ray absorption spectra with those from carefully chosen solid hydrates, supported by results from X-ray diffraction studies on solutions.<sup>[19]</sup> A similar study of the hydrated scandium(III) ion in solution is less straightforward, since only a few well-determined crystal structures are known of suitable solid hydrates<sup>[13,31,32]</sup> and the low atomic number causes experimental difficulties. The effective ionic radii for scandium(III) in six, seven and eight coordination (0.745, 0.80 and 0.87 Å, respectively) are derived from scandium(III) compounds with oxygen-donor ligands.<sup>[13]</sup> The Sc–O bond length for a hexaaquascandium(III) ion is expected to be around 2.08–2.09 Å, by adopting a radius of 1.34 Å for water as a ligand to the trivalent ion.<sup>[33]</sup> This estimate agrees well with the mean Sc–O distance of 2.08 Å obtained for octahedrally solvated scandium(III) ions, for example, in the crystal structures of  $[\text{Sc}(\text{H}_2\text{O})_6]\text{I}_3$ ,  $[\text{Sc}(\text{CH}_3\text{SO}_3)_6]\text{I}_3$ , and  $[\text{Sc}((\text{CH}_3)_2\text{SO})_6]\text{I}_3$ .<sup>[23,34]</sup> However, X-ray diffraction and EXAFS studies on the scandium(III) ion in aqueous solution result in a considerably longer mean Sc–O bond length, 2.17–2.18 Å, than that expected for six coordination, and the unusual hydration number of seven was proposed.<sup>[22,23]</sup> This interpretation is supported by the average Sc–O bond length of 2.16 Å that is found for the heptahydrated  $\text{Sc}^{3+}$  ions in the crystal structures of the hydrated halides,  $\text{ScX}_3 \cdot n\text{H}_2\text{O}$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ),<sup>[32]</sup> and in the “triflide” salt,  $[\text{Sc}(\text{H}_2\text{O})_7][\text{C}(\text{SO}_2\text{SCF}_3)_3]_3 \cdot \text{H}_2\text{O}$ , with the coordination figure described as a distorted monocapped trigonal prism.<sup>[35]</sup> Also, in the dimeric hydrolysis products,  $[\text{Sc}(\text{OH})_2(\text{OH})_5]_2\text{X}_4$  ( $X = \text{Cl}^-, \text{Br}^-$  and  $\text{PhSO}_3^-$ ), seven oxygen atoms surround the scandium(III) ion in monocapped trigonal prisms with mean Sc–O bond lengths of around 2.16 Å.<sup>[36,37]</sup>

With bidentate ligands, scandium(III) coordinates eight oxygen atoms in coordination polyhedra described as distorted dodecahedral or irregular bicapped trigonal prisms;<sup>[38]</sup> this occurs, for example, in the  $\text{HSc}(\text{O}_2\text{C}_7\text{H}_5)_4$  compound with a mean Sc–O bond length of about 2.21 Å.<sup>[39]</sup> Ninefold oxygen coordination also requires bidentate ligands,<sup>[20,31]</sup> even though a ninefold-hydrated  $[\text{Sc}(\text{H}_2\text{O})_9]^{3+}$  ion is assumed to exist, based on a previous crystal-structure determination for nonaqua scandium(III) trifluoromethanesulfonate.<sup>[8]</sup> In this hydrate, the site symmetry is consistent with a tricapped trigonal prism around the central scandium(III) ion with six short Sc–O<sub>p</sub> bond lengths of 2.171(6) Å, and three Sc–O<sub>c</sub> distances reported to be 2.47(2) Å. However, the stoichiometric composition was deduced only from the structural characterisation, and our redetermination of the structure revealed water deficiency.<sup>[23,25]</sup> Also, in a previous crystallographic study of the hydrated lutetium(III) trifluoromethanesulfonate a high thermal parameter of the capping oxygen

atoms was suggested to reflect a decrease in the coordination number.<sup>[6]</sup>

#### The low-temperature phase of the scandium hydrate, 1\*:

The refined thermal parameters of the scandium atom in the crystal structure of the hydrated scandium(III) trifluoromethanesulfonate **1** were remarkably high, as were those of the capping oxygen atoms. To explore this, the temperature was decreased stepwise and single-crystal data were collected at 293, 250, 200, 150 and 100 K. The thermal parameters decreased relatively uniformly for all atoms in the structure except for scandium, which showed a considerably smaller rate of change until about 188 K when a phase transition occurred. Examination of the reciprocal lattice of this low-temperature phase, **1\***, at 150 K and 100 K revealed a rhombohedrally centred unit cell approximately nine times larger than the one at ambient temperature. The unit-cell dimensions then increased three times in the *c* direction and by a factor of about  $\sqrt{3}$  in the *a* and *b* directions (Figure 4).

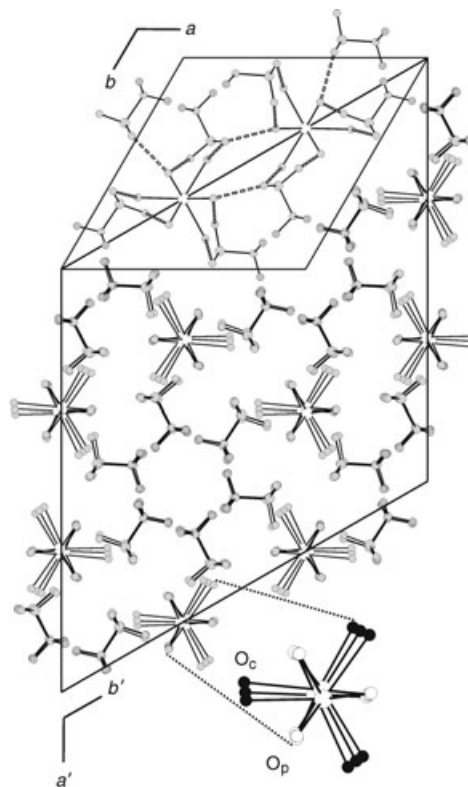


Figure 4. Relation between the unit cells of **1** at 293 K (smaller cell) and the low-temperature phase **1\*** at 150 K (larger cell), projected along the *c* axis. The cell edges increase by approximately three times in the *c* direction and with a factor of  $\sqrt{3}$  in the *a* and *b* direction at the 188 K phase transition.

Weak superstructure reflections in the layers  $l=2n+1$  and  $l=2n+2$  required the larger cell, while the strong main-structure reflections are only present in the  $l=3n$  layers. Several of the superstructure reflections were formally vio-



lating the reflection conditions for the chosen space group  $R\bar{3}$ . However, all symmetry-forbidden reflections could be explained by twinning, and the model in the space group  $R\bar{3}$  is expected to adequately represent the structure.

Alternatively, it was possible to describe  $\mathbf{1}^*$  in the space group  $P6_3/m$ , with the scandium atoms in two crystallographically different Sc sites. In one site, seven fully occupied and two less-than-half-occupied oxygen-atom positions would surround the scandium ion, while the other site displayed eight fully occupied oxygen positions and a ninth position with 27% occupancy. In the choice between the space groups  $R\bar{3}$  and  $P6_3/m$  the former is preferred, although a twin law has to be invoked in order to explain some of the reflections. However, the peculiar noncrystallographic absences exhibited (no superstructure reflections in the planes  $l=3n$ ) strongly suggest twinning, and the model in the  $R\bar{3}$

space group also yields a better  $R$  value, despite far fewer parameters (Table 3).

At 150 and 100 K, in the chosen space group  $R\bar{3}$ , seven oxygen atoms in fully occupied positions form a distorted monocapped trigonal prism with a mean Sc–O bond length of 2.19 Å, which is only slightly longer than the mean value of 2.16 Å found for heptahydrated scandium(III) ions in other structures.<sup>[32,35]</sup> Two more-distant capping water oxygen sites, Sc–O<sub>c</sub>(8) at 2.536(5) Å and Sc–O<sub>c</sub>(9) at 2.582(5) Å, with occupancy factors refined to 0.50 and 0.43, respectively, complete a distorted TTP polyhedron (Table 4).

The original unit cell was restored when the temperature was raised. Distinct features recorded with differential scanning calorimetry (DSC) confirmed the reversibility of the phase transition (Figure 5). Similar DSC measurements

Table 3. Crystallographic data for compounds **1**, **1\***, **2**, **3**, **4**, **5** and **6**.

	<b>1</b>	<b>1*</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
formula	C <sub>3</sub> H <sub>16.0</sub> F <sub>9</sub> O <sub>17</sub> S <sub>3</sub> Sc	C <sub>3</sub> H <sub>16.0</sub> F <sub>9</sub> O <sub>17</sub> S <sub>3</sub> Sc	C <sub>3</sub> H <sub>16.92</sub> F <sub>9</sub> O <sub>17.46</sub> S <sub>3</sub> Lu	C <sub>3</sub> H <sub>17.4</sub> F <sub>9</sub> O <sub>17.7</sub> S <sub>3</sub> Yb	C <sub>3</sub> H <sub>17.7</sub> F <sub>9</sub> O <sub>17.83</sub> S <sub>3</sub> Tm	C <sub>3</sub> H <sub>18</sub> F <sub>9</sub> O <sub>18</sub> S <sub>3</sub> Er	C <sub>3</sub> H <sub>18</sub> F <sub>9</sub> O <sub>18</sub> S <sub>3</sub> Tb
formula weight	636.30	636.30	774.60	776.99	775.34	776.61	768.27
crystal system	hexagonal	trigonal	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal
space group	$P6_3/m$	$R\bar{3}$	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$
$a$ [Å]	12.999(2)	22.411(2)	13.217(2)	13.290(3)	13.3984(10)	13.4622(16)	13.6599(11)
$c$ [Å]	7.7680(10)	23.070(2)	7.7440(10)	7.7810(10)	7.6955(5)	7.6672(10)	7.5589(5)
$\alpha, \beta, \gamma$ [°]	90, 90, 120	90, 90, 120	90, 90, 120	90, 90, 120	90, 90, 120	90, 90, 120	90, 90, 120
$V$ [Å <sup>3</sup> ]	1136.7(3)	10034.6(15)	1171.6(3)	1190.2(4)	1196.38(15)	1203.4(3)	1221.47(16)
$Z$	2	18	2	2	2	2	2
$T$ [K]	293	150	293	293	293	293	293
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]	1.859	1.895	2.196	2.168	2.152	2.143	2.089
$\rho_{\text{exptl}}$ [g cm <sup>-3</sup> ]	1.86(2)	–	2.19(2)	2.17(1)	2.14(2)	2.13(1)	2.09(1)
$\mu$ [mm <sup>-1</sup> ]	0.742	0.756	4.622	4.332	4.110	3.887	3.290
min/max $2\theta$	5.2/51.7	4.0/51.9	5.3/51.8	3.5/71.2	8.1/59.9	5.3/52.2	5.4/51.8
measured reflns	8734	12202	7717	14789	8955	9310	9541
unique reflns	786	4353	819	1848	1196	853	852
observed reflns	525	2663	746	860	792	780	797
$R_1/wR_2$	0.047/0.118	0.053/0.124 <sup>[a]</sup>	0.033/0.064	0.026/0.047	0.032/0.055	0.024/0.054	0.018/0.044
$[I > 2\sigma(I)]^{\text{[b]}}$							
$R_1/wR_2$ (all data)	0.073/0.130	0.088/0.137 <sup>[a]</sup>	0.039/0.066	0.094/0.052	0.068/0.060	0.028/0.056	0.020/0.045

[a] The standard deviation for unit-cell edges is as obtained from the refinements and does not include systematic errors (which were estimated from repeated measurements on **3** with different diffractometers to be about one magnitude larger). [b]  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum [w(F_o^2 - F_c^2)]^2] / \sum [w(F_o^2)]^2$ . [c] Modelling in space group  $P6_3/m$  at 150 K resulted in  $R_1 = 0.073$ ,  $wR_2 = 0.200$  for  $I > 2\sigma(I)$  and  $R_1 = 0.245$ ,  $wR_2 = 0.260$  for all data.

Table 4. Sc–O bond lengths to prism (O<sub>p</sub>) and capping (O<sub>c</sub>) water ligands, hydrogen-bond lengths to trifluoromethanesulfonate oxygen atoms (O<sub>t</sub>), and closest oxygen–oxygen contact distances O<sub>p</sub>...O<sub>p</sub> and O<sub>c</sub>...O<sub>p</sub> in the distorted capped trigonal prism of **1\***, [Sc(H<sub>2</sub>O)<sub>8.0</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, at 150 K (see Figure S3 in the Supporting Information).

Water oxygen O(x)	Sc–O(x) [Å]	O(x)–H...O <sub>t</sub> [Å]	O(x)...O(y) within triangular surfaces [Å]	O(x)...O(y) between triangles [Å]
O <sub>p</sub> (1)	2.169(2)	2.757(5), 2.769(4)	O(1)–O(3): 2.675(4), O(1)–O(5): 2.703(5)	O(1)–O(2): 2.729(3)
O <sub>p</sub> (2)	2.171(2)	2.790(4), 2.804(5)	O(2)–O(4): 2.688(5), O(2)–O(6): 2.704(5)	
O <sub>p</sub> (3)	2.193(3)	2.727(4), 2.784(3)	O(3)–O(1): 2.675(4), O(3)–O(5): <b>2.796(3)</b> <sup>[a]</sup>	O(3)–O(4): <b>3.092(4)</b> <sup>[c]</sup>
O <sub>p</sub> (4)	2.176(3)	2.717(4), 2.738(4)	O(4)–O(2): 2.688(5), O(4)–O(6): <b>2.790(4)</b> <sup>[a]</sup>	
O <sub>p</sub> (5)	2.146(3)	2.722(4), 2.728(4)	O(5)–O(1): 2.703(5), O(5)–O(3): 2.796(3)	O(5)–O(6): <b>3.089(4)</b> <sup>[c]</sup>
O <sub>p</sub> (6)	2.165(3)	2.729(4), 2.776(4)	O(6)–O(2): 2.704(5), O(6)–O(4): 2.790(4)	
O <sub>c</sub> (7)	2.291(3)	2.892(4), 2.893(4)	O(7)–O(5): 2.603(5), O(7)–O(3): 2.746(4), O(7)–O(6): 2.627(5), O(7)–O(4): 2.735(4)	
O <sub>c</sub> (8) <sup>[a]</sup>	2.536(5)	3.028(5), 3.055(5)	O(8)–O(5): 2.530(6), O(8)–O(1): 2.675(4), O(8)–O(6): 2.566(6), O(8)–O(2): 2.679(4)	
O <sub>c</sub> (9) <sup>[b]</sup>	2.582(5)	2.954(6), 2.963(5)	O(9)–O(3): 2.472(7), O(9)–O(1): 2.754(5), O(9)–O(4): 2.450(7), O(9)–O(2): 2.753(5)	

[a] Occupancy factor refined to 0.50(1). [b] Occupancy factor refined to 0.43(1). [c] Edges (bold) of the enlarged rectangular surface allowing the close approach of O<sub>c</sub>(7) to the scandium(III) ion.

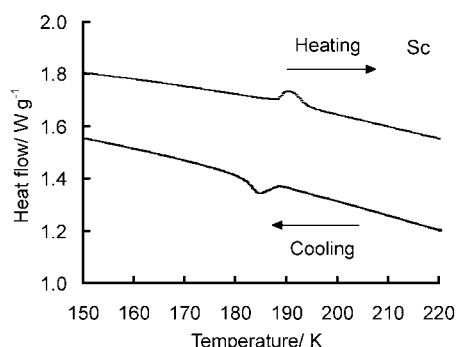


Figure 5. Differential scanning calorimetry (DSC) of  $[\text{Sc}(\text{H}_2\text{O})_{8.0}](\text{CF}_3\text{SO}_3)_3$  displays a reversible phase transition  $\mathbf{1} \rightleftharpoons \mathbf{1}^*$ , at about 188 K, which is exothermic when cooling;  $\Delta H^\circ = -0.80(1) \text{ kJ mol}^{-1}$ .

were then performed for the lanthanoid(III) compounds  $[\text{M}(\text{H}_2\text{O})_n](\text{CF}_3\text{SO}_3)_3$  with  $\text{M} = \text{Lu}, \text{Yb}, \text{Tm}, \text{Er}, \text{Ho}, \text{Dy}, \text{Y}$  and  $\text{La}$ ; phase transitions were found to occur at about 190 K for all the water-deficient compounds ( $\text{M} = \text{Sc}, \text{Lu}, \text{Yb}, \text{Tm}$  and  $\text{Er}$ ), with a weak effect also observed for the holmium(III) compound, while no phase transitions were indicated in this low-temperature range for the fully hydrated dysprosium(III), yttrium(III) and lanthanum(III) compounds.

**Hydrogen bonding and steric interactions:** The bridging hydrogen bonds contribute to stabilise the TTP geometry of the hydrated ions in the present isomorphous compounds. Two different oxygen atoms ( $\text{O}_i$ ) of each trifluoromethanesulfonate group accept hydrogen bonds from two TTP water molecules and form symmetric bridges between two  $\text{O}_p$  atoms along the threefold axis or asymmetric bridges between one  $\text{O}_p$  and one  $\text{O}_c$  atom, as shown in Figure 1. The significantly longer hydrogen bonds from the less-polarised water molecule in the capping position are still strong enough to pull the  $\text{O}_c$  atoms off the centre of the rectangular surfaces of the prism, an effect corresponding to a slight rotational displacement in the plane of the equatorial capping water molecules. The result is two longer and two shorter  $\text{O}_c \cdots \text{O}_p$  ligand–ligand contact distances (Table 1).

With decreasing radius in the series of lanthanoid(III) ions, the edge of the equatorial triangle of the prism decreases until the  $\text{O}_p \cdots \text{O}_p$  ligand–ligand repulsion resists further contraction. The axial contraction of the trigonal prism continues, with the bridging axial hydrogen bonds donated by  $\text{O}_p$  atoms holding the triangular surfaces in an eclipsed alignment. The effect can be seen in Table 1, in which the closest  $\text{O}_p \cdots \text{O}_p$  distance obtained within the triangular sides of the prism decreases from 2.865(4) Å, through 2.844(6), 2.842(4) and 2.846(7) Å, to 2.748(4) Å for Er, Tm, Yb, Lu, and Sc, respectively. This can be compared with the contact  $\text{O}_c \cdots \text{O}_p$  distances, which are even shorter (2.677(4), 2.663(5), 2.663(4), 2.641(8) and 2.561(6) Å, respectively). The  $\text{O}_p \cdots \text{O}_p$  and  $\text{O}_c \cdots \text{O}_p$  distances are those obtained for the crystallographic TTP positions.

The increasing  $\text{O}_c \cdots \text{O}_p$  ligand–ligand repulsion of the contracting trigonal prism even causes the  $\text{M}-\text{O}_c$  distance to in-

crease for some of the smallest lanthanoid ions (Table 1). Eventually, the release of one capping water, thereby allowing the metal ion to approach the remaining capping oxygen atoms while keeping the  $\text{M}-\text{O}_p$  distances almost unchanged by distorting the trigonal prism, becomes more favourable than the fully occupied regular TTP coordination geometry. The phase transitions shown by DSC measurements for all the water-deficient hydrates probably reflect a transformation from a regular TTP prism to a distorted capped configuration at low temperature ( $\approx 190 \text{ K}$ ), as for the scandium  $\mathbf{1}^*$  compound. This is consistent with the almost constant  $\text{O} \cdots \text{O}$  contact distances for the smallest lanthanoid(III) ions in the series, for which the inherent instability for coordinating three equidistant capping oxygen atoms should decrease with increasing ionic radii. The smallest stable TTP cage of water molecules around a trivalent metal ion should then be given by  $\text{O}_p \cdots \text{O}_p$  distances of 2.87 and 3.31 Å within and between the triangular surfaces of the trigonal prism, respectively, and by an  $\text{O}_c \cdots \text{O}_p$  contact distance of 2.68 Å for the capping oxygen atoms, that is, slightly larger dimensions than those for the hydrated erbium(III) ion.

In the low-temperature phase  $\mathbf{1}^*$  of the hydrated scandium(III) trifluoromethanesulfonate, one rectangular surface of the distorted trigonal prism has expanded (see Tables 1 and 4) to allow the close approach of one capping water oxygen ( $\text{Sc}-\text{O}_c(7)$ : 2.291(3) Å). The contraction of the two other sides of the prism then forces the two corresponding capping sites outward ( $\text{Sc}-\text{O}_c(8)$  and  $\text{Sc}-\text{O}_c(9)$ : 2.536(5) and 2.582(5) Å, respectively). The mean contact distance between the capping oxygen atom for the fully occupied site and the four atoms of the rectangular surface ( $\text{O}_c(7) \cdots \text{O}_p$ : 2.68 Å) is actually equal to the  $\text{O}_c \cdots \text{O}_p$  distance established for a stable TTP cage (see above), while for both the half-occupied sites,  $\text{O}_c(8)$  and  $\text{O}_c(9)$ , a shorter mean  $\text{O}_c \cdots \text{O}_p$  distance of 2.61 Å is obtained (see Table 4).

The hydrogen bonding in  $\mathbf{1}^*$  also reflects the different  $\text{Sc}-\text{O}$  bond strengths in the distorted coordination polyhedron. The 12 hydrogen bonds,  $\text{O}_p(\text{H}) \cdots \text{O}_i$ , from the tightly bonded prism water molecules to the surrounding trifluoromethanesulfonate oxygen atoms remain short and are all in the range of 2.72–2.80 Å (see Table 4 and Figure S3 in the Supporting Information). However, the hydrogen bonds from the fully occupied capping water site,  $\text{O}_c(7)(\text{H}) \cdots \text{O}_i$  ( $2 \times 2.89$  Å), are shorter than those from the more distant sites  $\text{O}_c(8)(\text{H}) \cdots \text{O}_i$  (2.95 and 2.96 Å) and  $\text{O}_c(9)(\text{H}) \cdots \text{O}_i$  (3.03 and 3.06 Å). This is consistent with the shortening of the  $\text{Sc}-\text{O}_c(7)$  bond, which increases the polarisation of the  $\text{O}_c(7)$  water molecule and thereby the hydrogen-bond strength.

**$^2\text{H}$  NMR spectroscopy studies of water mobility:** The reversible phase transition of the scandium hydrate and the equivalent capping positions in the crystal structure above the transition temperature indicated that the coordinated water molecules could exchange positions in the TTP hydrates, even in the solid state. The water mobility was therefore studied by means of  $^2\text{H}$  solid-state NMR spectroscopy



on the diamagnetic  $[M(^2\text{H}_2\text{O})_n](\text{CF}_3\text{SO}_3)_3$  salts with  $M = \text{Sc}$ , Lu, Y or La, within the temperature range 268–358 K. The isomorphous fully hydrated yttrium(III) and lanthanum(III) hydrates of Group 3 with closed-shell electron structures were chosen for comparison with the water-deficient scandium(III) and lutetium(III) compounds, since we could not obtain useful spectra of the ytterbium(III), thulium(III) and holmium(III) hydrates because of the paramagnetism of the unpaired 4f electrons.

The  $^2\text{H}$  NMR spectra of the four hydrates exhibit three types of spectral features (Figure 6):

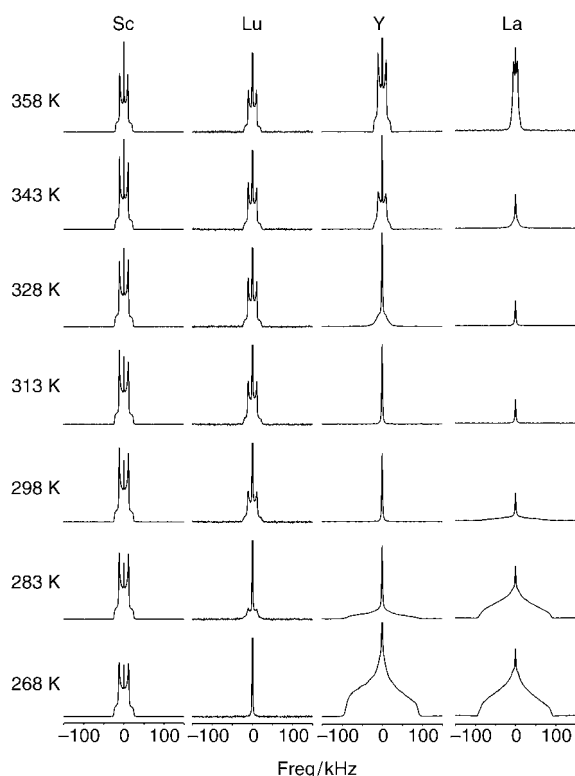


Figure 6.  $^2\text{H}$  solid-state NMR spectra of  $[M(^2\text{H}_2\text{O})_n](\text{CF}_3\text{SO}_3)_3$  hydrates, with  $M = \text{Sc}$ , Lu, Y and La, in the temperature range 268–358 K. The sharp peak at zero frequency originates from noncoordinated surface water. The broad features at low temperatures for the yttrium(III) and lanthanum(III) hydrates are characteristic of a rapid twofold rotation of coordinated water. The narrow powder patterns, with a width  $\approx 40$  kHz, indicate positional exchange of the water molecules.

- A sharp peak at zero frequency in all spectra indicates isotropically reorientating deuterons and can be ascribed to noncoordinated water on the surface of the crystals. These sharp peaks are of comparable magnitude in all spectra, a result indicating that the amount of noncoordinated water stays the same during the temperature variations for compounds in the closed containers.
- The broad powder pattern, with an overall width of  $\approx 170$  kHz and an asymmetry parameter of  $\approx 1$ , that occurs at low temperatures for the yttrium(III) and lanthanum(III) hydrates is characteristic of a rapid two-

fold rotational twist around the M–O bond of the coordinated water molecule.<sup>[40]</sup>

- For all scandium(III) and most lutetium(III) spectra, and also for the high-temperature yttrium(III) and lanthanum(III) spectra, rather narrow powder patterns with widths of  $\approx 40$  kHz and asymmetry parameters of  $\approx 0$  are observed.

In order to interpret these spectra in terms of water mobility, we consider first the yttrium and lanthanum compounds. At low temperature, the broad line shape (feature b) appears when the coordinated water molecules perform a fast rotational-flip motion in their lattice positions. When the temperature increases, the intensity of this broad spectral feature decreases. This indicates the onset of a new dynamic process with a rate comparable to the strength of the rigid-lattice  $^2\text{H}$  quadrupolar interaction, which is  $\approx 10^5 \text{ s}^{-1}$ .<sup>[41]</sup> Eventually, when the temperature is sufficiently high, the rate of this motion becomes fast ( $\gg 10^5 \text{ s}^{-1}$ ) on the  $^2\text{H}$  NMR timescale and the relatively narrow powder pattern (feature c) emerges. In accordance with the assignments in previous investigations of hydrated solids,<sup>[42]</sup> we associate this feature with positional exchange of the water molecules.

The single exchange-averaged  $^2\text{H}$  pattern (feature c) indicates that the water molecules in all TTP sites, prism and capping, become mobile around the metal ions when the temperature is raised. For the yttrium(III) and lanthanum(III) hydrates, fast exchange begins at about 330 and 360 K, respectively. The water dynamics observed for the scandium(III) and lutetium(III) hydrates are similar, even though fast exchange has already started at about 280 K for lutetium(III) and below the lowest measuring temperature of 268 K for the hydrated scandium(III) ion. Hence, for these two compounds the higher number of vacant capping positions corresponds to a higher water mobility at a given temperature.

**Positional exchange of water molecules:** The results from the  $^2\text{H}$  NMR spectroscopy studies indicate an inversion mechanism in all of the investigated solid hydrates that allows, at sufficiently high temperature, rapid positional exchange of water molecules between the prism and capping oxygen atom positions in the TTP configuration. The prism positions are more favoured because of the stronger M–O<sub>p</sub> bonds,<sup>[24]</sup> and will always appear fully occupied in the crystal structure, while the distribution of vacancies in the capping positions becomes equivalent due to the mobility. Even though water deficiency appears to lower the temperature required for fast exchange, vacancies are not necessary for exchanging the positions of the coordinated water molecules. The reason why rapid water exchange for the fully nonhydrated lanthanum(III) ion starts at a higher temperature than that for the smaller, likewise-nonhydrated yttrium(III) ion with higher electrostatic M–O attraction may be the stronger hydrogen bonding to the capping water molecules (Table 1). The hydrogen-bonded distances from the capping water molecules to the oxygen atoms of the trifluoromethanesulfonate ions, O<sub>c</sub>···O<sub>p</sub>, are shorter for

lanthanum(III) (2.932(4) Å) than for yttrium(III) (3.004(5) Å), and the distances are most equal for the prism water molecules, with  $O_p \cdots O_t$  distances of 2.755(5) and 2.840(2) Å for lanthanum(III) and of 2.750(6) and 2.830(3) Å for yttrium(III).

The MD simulation studies of Kowall et al. of the dynamic behaviour of the first hydration shell of the lanthanoid(III) aqua ions described the polarisable potential of the water molecules by scaling the cation–water and water–water Coulomb interactions with a distance-dependent factor.<sup>[16]</sup> In a preliminary step the energies were minimised for coordination polyhedra with nine water molecules arranged in  $C_{2v}$  symmetry on the surface of a sphere, with the water molecules strictly radially aligned. The energy minima correspond to different orientations of the trigonal axis in TTP hydrates and are separated by a saddle point with only 1.2 kJ mol<sup>-1</sup> higher energy, a point corresponding to the monocapped square antiprismatic geometry. An inversion movement along the valley in the potential energy surface between the trigonal prismatic configurations would scramble all nine atoms in such a model, since any one of the three capping atoms of the trigonal prism can become the capping atom of the square antiprism. However, such a change from one TTP orientation to another would correspond to a 90° reorientation of the sixfold inversion axis of the prism, which is not allowed within the lattice of the crystal structure. In the MD study by Floris and Tani, in which *ab initio* effective pair potentials were used, other internal rearrangements of the hydrating water molecules were also found to occur; these molecules were performing rather localised motions due to the combination of strong ion–water attraction and harsh water–water repulsion.<sup>[18]</sup>

For the TTP hydrated ions with water deficiency, a prism oxygen atom moving to a vacant capping position would leave a hole which then can be filled with the adjacent capping oxygen atom (Figure 7). However, for the nonaqua yttrium(III) and lanthanum(III) ions and for other fully hydrated ions, for example part of the hydrated lutetium(III) ions, a conceivable mechanism for the observed water mobility would require a simultaneous 90° twist of the atoms in the lower square plane in an antiprism capped by the top-most water molecule, as indicated in Figure 7. When the hydrated metal ion relaxes back to the crystallographic TTP position, the twist would have caused an exchange between prism and capping water molecules consistent with the <sup>2</sup>H NMR spectra.

**Lewis acidity and capping sites:** The ytterbium(III) trifluoromethanesulfonate (“triflate”) is the most useful of the lanthanoid(III) trifluoromethanesulfonates as a water-tolerant Lewis acid for catalysing many types of organic syntheses, although in the last decade the lanthanide-like scandium(III) trifluoromethanesulfonate has been found to be even more efficient.<sup>[12,13]</sup> For example, solutions of the small scandium(III) and ytterbium(III) ions were found to be significantly more efficient as recyclable catalysts in the nitration of aromatic compounds in organic solvents than the

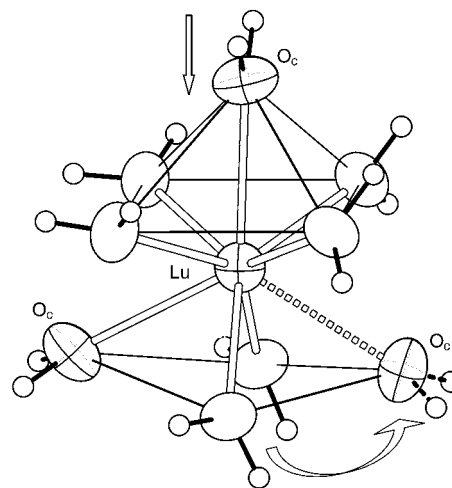


Figure 7. Proposed mechanism for positional exchange of the prism ( $O_p$ ) and capping ( $O_c$ ) water molecules in TTP hydrates. The monocapped square antiprismatic configuration allows twisting of the lower plane, facilitated by water deficiency, as displayed for the  $\text{Lu}(\text{H}_2\text{O})_9^{3+}$  ion. The ellipsoids enclose 50% electron density.

lanthanum(III), praseodymium(III) and europium(III) trifluoromethanesulfonates.<sup>[35,43]</sup> The reaction produces water molecules that will expel trifluoromethanesulfonate ions from the first coordination sphere in a mixed reaction medium.<sup>[44]</sup> “The compatibility of lanthanoid(III) triflate salts with water and yet their apparent ability to function as strong Lewis acids is somewhat paradoxical.”<sup>[43]</sup> Bridging hydrogen bonding from the coordinated water molecules to trifluoromethanesulfonate ions could be able to stabilise a trigonal prism around such partially hydrated scandium and lanthanoid(III) ions. Especially for the small scandium(III) and ytterbium(III) ions, the donor atoms of the substrate molecules would be able to compete favourably with the bulky organic solvent molecules for ligating the metal ion in the capping positions.

This is also indicated by an MD study of the ytterbium(III) hydration, which concluded that “even a light perturbation could rather easily remove the capping water in the hydration shell of  $\text{Yb}^{3+}$ .”<sup>[18]</sup> When trifluoromethanesulfonate is exchanged for the bulky tris(trifluoromethanesulfonyl)methide (“triflide”) anion for ytterbium(III) and scandium(III),  $[\text{Yb}/\text{Sc}(\text{OH}_2)_n] \cdot \text{H}_2\text{O}$  units encapsulated by the triflide anions can crystallise from aqueous solutions, in isomorphous salts with  $n=8$  for ytterbium(III) and  $n=7$  for scandium(III).<sup>[34]</sup> The arrangement of water around these hydrated cations can be described as distorted bi- and monocapped trigonal prisms, respectively. There is a “dramatic increase in activity of the triflide salts versus the corresponding triflates for the aromatic nitration of the electron-deficient arene *o*-nitrotoluene”.<sup>[35]</sup> Presumably, this higher catalytic activity is an effect of the more flexible coordination sphere increasing the accessibility to the metal ion and thus increasing the ion’s effectiveness as a Lewis acid.

Competition between anions and capping water molecules is probably the reason why the hydration number of the lutetium(III) ion shows strong concentration dependence in

water/acetone mixtures, as found by the NMR spectroscopy peak-area method.<sup>[17]</sup> When the aqueous concentration of  $\text{Lu}(\text{ClO}_4)_3$  was increased, from relatively dilute ( $0.49 \text{ mol dm}^{-3}$ ) to highly concentrated ( $2.9 \text{ mol dm}^{-3}$ ) solutions, the number of water molecules coordinated to the lutetium(III) ion decreased gradually from  $8.7 \pm 0.45$  to  $6.3 \pm 0.12$ .

## Conclusion

This study provides very clear-cut examples that ionic size and ligand–ligand interactions are the main factors determining the arrangement of aqua ligands around highly hydrated trivalent metal ions. However, for crystalline hydrates, directed hydrogen bonding to the neighbouring anionic species is shown to influence not only the configuration but also the hydration number.

Water deficiency was found for the smallest hydrated trivalent metal ions surrounded by tricapped trigonal prisms of nine water molecules in the isomorphous series of trifluoromethanesulfonates,  $[\text{M}(\text{H}_2\text{O})_n](\text{CF}_3\text{SO}_3)_3$  in which  $\text{M} = \text{Sc}, \text{Lu}, \text{Yb}, \text{Tm}$  or  $\text{Er}$ . Crystallographic refinement of occupancy factors at ambient temperature yielded the number of water molecules per metal ion (the hydration number,  $n = 8.02(4), 8.43(8), 8.72(3), 8.84(5)$  and  $8.96(5)$ , respectively) and located the water deficiency to the capping positions. Residual electron density in the plane of the capping oxygen atoms in the prism indicates that the vacancies are randomly distributed in the crystal structure. The repulsion from the prism oxygen atoms hampers the approach of the capping oxygen atoms toward the trivalent metal ions. Lanthanoid(III) ions with a lower atomic number than erbium(III) are sufficiently large to keep a regular TTP geometry with three capping water molecules by expanding the sides of the prism. However, for the smaller ions, including scandium(III), a configuration with one vacant capping position and with the metal ion displaced toward the remaining capping water oxygen atoms in a distorted prism can become more favourable.

DSC measurements showed exothermic phase transitions for all the water-deficient trifluoromethanesulfonate compounds,  $[\text{M}(\text{H}_2\text{O})_n](\text{CF}_3\text{SO}_3)_3$  with  $\text{M} = \text{Sc}, \text{Lu}, \text{Yb}, \text{Tm}$  or  $\text{Er}$ , when they were cooled below about 190 K. Single-crystal data at 150 and 100 K showed that the  $[\text{Sc}(\text{H}_2\text{O})_{8.0}](\text{CF}_3\text{SO}_3)_3$  compound reversibly transformed to a trigonal cell that was almost nine times larger, with the scandium ion surrounded by seven fully occupied oxygen atom positions (mean Sc–O distance of  $2.19 \text{ \AA}$ ) and another two half-occupied distant positions, in a distorted capped trigonal prism (see Figures 4 and 5 and Figure S3 in the Supporting Information). The phase transitions are probably triggered by the instability of the TTP configuration around the small metal ions, with the three equidistant capping oxygen atoms being strongly repelled by the prism oxygen atoms.

The high symmetry, with equivalent water deficiency in the capping oxygen positions at ambient temperature, prompted a  $^2\text{H}$  solid-state NMR spectroscopy study of the

mobility of the water molecules in the coordination sphere, which was feasible for the diamagnetic compounds  $[\text{M}(\text{H}_2\text{O})_n](\text{CF}_3\text{SO}_3)_3$  with  $\text{M} = \text{Sc}, \text{Lu}, \text{Y}$  and  $\text{La}$ . The temperature for which the positional exchange of coordinated water molecules between capping and prism positions became rapid on the  $^2\text{H}$  NMR timescale ( $\geq 10^5 \text{ s}^{-1}$ ) was lowest for the scandium(III) compound, at below 268 K. For lutetium(III), with fewer vacant oxygen positions, the positional exchange becomes rapid above about 280 K; for the large yttrium(III) and lanthanum(III) ions, without vacancies, the NMR spectra indicate rotational-flipping motions of the water molecules at temperatures below about 283 K but also rapid exchange of their positions at elevated temperatures, above 330 and 360 K, respectively. In crystallographic studies over the phase-transition temperature, the more favoured prism positions, with shorter M–O bond lengths and longer residence times, will always appear fully occupied for the water-deficient compounds.

The relatively strong hydrogen bonding to the anions evidently has an important role in stabilising the TTP cage around trivalent metal ions with such a large range of ionic radii as in the series of isomorphous trifluoromethanesulfonate hydrates. Two oxygen atoms of each sulfonate group bridge hydrogen bonds from two water molecules in the TTP hydrate, and the coordinated water molecules are held together in pairs along the threefold axis in the trigonal prism (see Figure 1). Such a hydrogen-bond arrangement certainly favours the trigonal prism of six water molecules as a building block for hydration numbers exceeding six, by allowing close approach of capping waters or other ligands at the rectangular surfaces. This is probably the main reason why the relatively small scandium(III) ion can obtain the high hydration number of about eight in the hydrated scandium(III) trifluoromethanesulfonate, while the hydration number is only seven in the halides with weaker hydrogen bonds<sup>[32]</sup> and six for the hydrated methanesulfonate  $[\text{Sc}(\text{H}_2\text{O})_6][\text{Sc}(\text{CH}_3\text{SO}_3)_6]$  with strong hydrogen bonding but in a different arrangement.<sup>[19]</sup> Also, the efficiency especially of scandium(III) trifluoromethanesulfonate as a water-tolerant Lewis acid catalyst for many organic syntheses<sup>[12,13]</sup> is possibly connected to the potential for the donor atoms of the substrate molecules to bind to the metal ion in the capping positions of a trigonal prism.

## Experimental Section

**Syntheses and analyses:** Colourless hexagonal rodlike crystals,  $[\text{M}(\text{H}_2\text{O})_n](\text{CF}_3\text{SO}_3)_3$  in which  $\text{M} = \text{Sc}$  (**1**),  $\text{Lu}$  (**2**),  $\text{Yb}$  (**3**),  $\text{Tm}$  (**4**),  $\text{Er}$  (**5**) or  $\text{Tb}$  (**6**), formed when slowly evaporating acidic ( $\text{pH} \approx 1$ ) aqueous solutions of the trifluoromethanesulfonate salts. The solutions were prepared by dissolving the oxides,  $\text{M}_2\text{O}_3$ , in diluted trifluoromethanesulfonic acid,  $\text{HCF}_3\text{SO}_3$  (Fluka), whilst stirring and heating. The slightly hygroscopic crystals were enclosed in glass capillaries during the diffraction experiment. For  $^2\text{H}$  solid-state NMR measurements, crystals of  $[\text{M}(^2\text{H}_2\text{O})_n](\text{CF}_3\text{SO}_3)_3$  in which  $\text{M} = \text{Sc}, \text{Lu}, \text{Y}$  or  $\text{La}$ , with  $> 99\%$  deuteration were prepared by repeated ( $> 3$  times) evaporation and recrystallisation of  $^2\text{H}_2\text{O}$  solutions of the hydrated trifluoromethanesulfonate salts.

The number of water molecules per metal ion was determined by several methods. Crystallographic refinement of the oxygen occupancy parameters and density measurements by means of flotation in  $\text{CCl}_4 + \text{CBr}_4$  mixtures were performed in all cases (Table 2), and thermogravimetric analysis (TGA) was also carried out by using a Perkin–Elmer TGA7 Analyzer (Figure S2 in the Supporting Information). The weight loss was monitored when heating the sample (about 20 mg) at a rate of  $10 \text{ K min}^{-1}$  from 293 to 573 K, under a constant flow of dry air. DSC, by means of a Perkin–Elmer DSC Pyris 1 instrument, was used to detect phase transitions by monitoring the energy absorbed or released when small amounts of the crystalline samples ( $\approx 10 \text{ mg}$ ) were cooled from 293 to 133 K at a rate of  $10 \text{ K min}^{-1}$  and then the temperature was allowed to increase to 293 K.

**$^2\text{H}$  NMR spectroscopy:** Deuterium solid-state NMR spectra were acquired with a Chemagnetics Infinity 400 MHz spectrometer (9.4 T) by using the quadrupolar echo sequence.<sup>[45]</sup> The  $^2\text{H}$   $\pi/2$  pulse duration was 1.8  $\mu\text{s}$ , and the recycle delay was always at least 5 times the spin-lattice relaxation time. The first echo delay was set to 50  $\mu\text{s}$ , and the second delay was carefully chosen so that the first point in the free induction decay was digitised at the spin-echo maximum. The deuterated crystalline samples were contained in a closed Teflon container and checked to ensure that no weight loss occurred. The temperature was cycled to ensure that the same spectra were obtained when returning to the starting temperature. A detailed discussion of motional effects on  $^2\text{H}$  solid-state NMR spectra can be found elsewhere.<sup>[41]</sup>

**X-ray crystallography:** Data were collected at ambient temperature with single crystals of **1–6** and at low temperature (100 and 150 K) with  $[\text{Sc}(\text{H}_2\text{O})_9](\text{CF}_3\text{SO}_3)_3$  (**1\***) by means of a STOE IPDS diffractometer equipped with an imaging-plate detector. For the ytterbium(III) hydrate (**3**), data were also collected with a STOE AED2 four-circle diffractometer; for the thulium(III) hydrate (**4**), an Oxford Instruments Xcalibur diffractometer equipped with a CCD detector and CrysAlis software was employed. The STOE IPDS software package was used for indexing and integrating the single-crystal reflections. Absorption corrections were performed with the programs X-RED and X-SHAPE, by using symmetry-equivalent reflections to model crystal shape and size.<sup>[46]</sup> The structures were solved by using SHELXS97 direct methods and were refined with SHELXL97 program by applying full-matrix least squares on  $F^2$ .<sup>[47]</sup> All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the water molecules were located from the residual density map and their positional parameters were refined. For **1** and **1\***, a tight restraint of the O–H bond length was introduced and the H...H distance was kept at a value corresponding to the H–O–H angle of  $104.5^\circ$ . This way of modeling allows reorientations of almost rigid water molecules, as no riding atom model is available for water molecules in the SHELXL97 program. Molecular structure visualisations were performed by means of the DIAMOND program,<sup>[48]</sup> and the electron density maps were obtained by means of the PLATON program.<sup>[49]</sup> Selected crystallographic and experimental details are summarised in Table 4.

The Supporting Information for this article contains anisotropic temperature factors ( $\text{\AA}^2$ ) for the non-hydrogen atoms of the tricapped trigonal  $[\text{M}(\text{H}_2\text{O})_9]^{3+}$  ions (Table S1), excess electron-density maps around prism oxygen atoms for the scandium compound (Figure S1), TGA and DSC curves for the hydrated scandium(III), yttrium(III) and lanthanum(III) trifluoromethanesulfonates (Figure S2) and a DIAMOND<sup>[48]</sup> picture of the hydrogen bonding in the low-temperature phase **1\*** of the hydrated scandium(III) trifluoromethanesulfonate (Figure S3).

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository CSD numbers (filename): 415177 (Sc-triflate-293.cif), 415178 (Sc-triflate-250.cif), 415179 (Sc-triflate-200.cif), 415180 (Sc-triflate-150.cif), 415181 (Sc-triflate-100.cif), 415182 (Lu-triflate.cif), 415183 (Yb-triflate.cif), 415184 (Tm-triflate.cif), 415185 (Er-triflate.cif) and 415186 (Tb-triflate.cif).

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