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Crystal Structures of Hydrated Rare-Earth Bis(trifluoromethylsulfonyl)imide Salts

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Crystals of hydrated bis(trifluoromethylsulfonyl)imide (Tf_2N) salts of the naturally occurring trivalent rare-earth ions we grown from aqueous solution and analysed by X-ray diffraction. Their structures can be classified into three main groups. The lighter lanthanides La–Gd (except Sm) have a cubic crystal structure with the formula $Ln(H_2O)_3(Tf_2N)_3$, which has Tf_2 anions coordinating in a bidentate fashion. The middle and heavy lanthanides (Sm, Tb, Dy, Er, Yb) have a monoclinic crystal structure with formula $Ln(H_2O)_5(Tf_2N)_3$, where the Tf_2N anions are coordinating in a monodentate fashion. The heavy lanthanides Gd–Lu (except Tb, Tm) crystallise with very large unit cells making structural identification difficult. Partial structure solution of one of these compounds indicates that the structures contain fully hydrated Ln^{3+} ions and very disorderd Tf_2N anions. Y was found to behave as the heavy lanthanides and Sc was found in a crystal structure of formula $[Sc(H_2O)_7][Tf_2N]_3{\cdot}H_2O$. In addition, La was found in a hexagonal crystal structure of formula $La(H_2O)_3(Tf_2N)_3{\cdot}2.5H_2O$, when a small amount of residual HTf_2N was present during crystallisation.

Introduction

The fifteen lanthanides plus scandium and yttrium are called the rare earths. These elements are used in a growing number of applications such as strong permanent magnets, lamp phosphors, rechargeable batteries, ceramics, catalyst, etc.[1] During the last few years, the rare-earth supply in the United States and the European Union has been under pressure, due to the export quota of China, which is the largest producer or rare-earth oxides.[2-4] The recent rare-earth crisis and the increasing use of rare earths are the major reasons for an increasing interest in these elements, ranging from fundamental research towards recycling programs and investments in the reopening of old rare-earth mines.[5-7]

The super acid hydrogen bis(trifluoromethylsulfonyl)imide (HTf_2N) was described the first time in 1984.[8] The Tf_2N anion is a weakly coordinating anion due to a proper delocalisation of the -1 charge over the entire anion. Therefore, the intermolecular interactions with other molecules and, more specific with cations, are reduced.

Ionic liquids are defined as compounds that consist entirely of ions.[9-11] The Tf_2N anion is very popular in applications were ionic liquids are used because it forms ionic liquids with low melting points and low viscosities. Moreover, it forms hydrophobic ionic liquids that are stable against hydrolysis, unlike other hydrophobic BF_4 and PF_6 ionic liquids.[12] The anion is frequently chosen in ionic liquids that are used as electrolytes in lithium batteries.[13-15] The hydrophobic Tf_2N anion is also often incorporated in solvent extraction systems where ionic liquids are used as hydrophobic organic phase.[16-20] Sometimes, ion exchange can be avoided in some systems by choosing the Tf_2N anion to charge-balance the metal cation. Ionic liquids comprising a metal cation that is coordinated by several neutral ligands such as acetonitrile or *N*-alkylimidazoles and charge balanced by non- or weakly coordinating anions such as Tf_2N are liquid metal salts with low melting points.[22-25] The incorporation of the metal in the cation of the liquid metal salt makes it easier to electrodeposit the metal on the negatively charged cathode.[22-25] Metal bis(trifluoromethylsulfonyl)imides have also been used as Lewis acid catalyst in organic synthesis.[26-31] For example, Suzuki *et al*. found that $Yb(Tf_2N)_3$ catalyzed Michael reactions of beta-ketoesters[27] and Duris *et al*. showed that $La(Tf_2N)_3$ acted as catalysts for Friedel-Crafts acylations.[30]

There have been several reports of anhydrous rare-earth bis(trifluoromethylsulfonyl)imide complexes with and without other counter ions.[32] For example, Mudring *et al*. reported on homoleptic compounds of trivalent lanthanides with the counteranion 1,1-butylmethylpyrrolidinium (bmpyr) and found either four or five coordinating Tf_2N anions depending on the size of the Ln^{3+} cation: $[bmpyr]_2[Ln(Tf_2N)_5]$ (Ln = Nd, Tb) and $[bmpyr][Ln(Tf_2N)_4]$ (Ln = Tm, Lu).[32a] Four crystal structures of hydrated rare-earth bis(trifluoromethylsulfonyl)imides have so far been described for the rare earths. The structure of $La(H_2O)_3(Tf_2N)_3$ was reported by Bhatt *et al.*[33] and contains

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† Electronic Supplementary Information (ESI) available: full experimental, additional views of the crystal structures and sample diffraction images. See DOI: 10.1039/x0xx00000x

three coordinated water molecules and three bidentate Tf_2N anions. Kawamura *et al.* reported the crystal structures of $Eu(H_2O)_3(Tf_2N)_3$, $Eu(H_2O)_3(Tf_2N)_3$·docosane and $Yb(H_2O)_5(Tf_2N)_3$ grown from *p*-xylene solutions.[34] In this study, Kawamura *et al.* started from anhydrous metal salts and used the medium *p*-xylene for the crystal synthesis along with the stoichiometric amounts of water and other strange additives such as heptanoic acid and docosane. They found that $Eu(H_2O)_3(Tf_2N)_3$ was isostructural with the La analogue reported by Bhatt *et al.* but could be found in another phase with a channel structure. The structure of $Yb(H_2O)_5(Tf_2N)_3$ contained the bis(trifluoromethylsulfonyl)imide anions coordinated in a monodentate fashion. In our study, we systematically investigated the formation of the rare-earth bis(trifluoromethylsulfonyl)imide salts in an aqueous medium and their crystallisation properties *in vacuo*. The crystal structures of hydrated rare-earth bis(trifluoromethylsulfonyl)imides from the whole series rare-earths are reported and compared to each other and to the structures described in the literature.

Experimental

Materials and methods

An 80 wt% solution of the acid hydrogen bis(trifluoromethylsulfonyl)imide was purchased from Iolitec (Heilbronn, Germany). Pr_6O_{11} (99.99%) and Nd_2O_3 (99.99%) were obtained from Alfa Aeser (Karlsruhe, Germany). Sc_2O_3 (99.99%), Sm_2O_3 (99.99%) Gd_2O_3 (99.99%) and Er_2O_3 (99.99%) were purchased from Rare Earth Products Limited (Beverly, USA). Tm_2O_3 (99.9%) was obtained from GFS Chemicals (Powell, Ohio, USA). La_2O_3 (99.99%), Dy_2O_3 (99.99%) and $Ce_2(CO_3)_3$ (99.9%) were obtained from Sigma-Aldrich (Diegem, Belgium) All chemicals were used without further purification. The synthesised crystals could not be characterised by other techniques than X-ray diffraction as they are highly hygroscopic.

The crystals were synthesised by the general procedure: the rare-earth oxide was added in excess to a 80 wt% hydrogen bis(trifluoromethylsulfonyl)imide solution along with 30 mL of water in a sealed vial unless otherwise reported. The mixture was heated to 80 °C usually for one or two hours. Unreacted oxide was separated by filtration and the water was removed from the filtrate by rotary evaporation. For full details for each compound see the ESI.

Crystallography

Crystals of $[Sc(H_2O)_7][Tf_2N]_3·H_2O$, $Ce(H_2O)_3(Tf_2N)_3$, $Pr(H_2O)_3(Tf_2N)_3$, $Nd(H_2O)_3(Tf_2N)_3$, $Gd(H_2O)_3(Tf_2N)_3$, $Sm(H_2O)_5(Tf_2N)_3$, $Tb(H_2O)_5(Tf_2N)_3$, $Dy(H_2O)_5(Tf_2N)_3$, $Er(H_2O)_5(Tf_2N)_3$ and $La(H_2O)_3(Tf_2N)_3·2.5H_2O$ were quickly removed from the reaction vessel and placed on a glass slide. Then very quickly using a nylon loop mounted on a copper pin, a suitable crystal was selected and placed in the cold stream of an Oxford Cryostream 700 at 100(2) K on an Agilent SuperNova diffractometer using Mo Kα radiation (λ = 0.71073 Å). The absorption corrections were applied using CrysAlisPro.[35] All structures were solved using direct methods and refined by the full-matrix least-squares procedure in SHELXL.[36] For refinement and making pictures, the program OLEX2 was used.[37] Hydrogen atoms were found in the difference map and the O–H distances fixed to be 0.84 Å. In the structures where H atoms could not be found in the difference map they were omitted from the refinement but kept in the final formula. A summary of the pertinent data for each crystal is given in Table 1 and pictures of the asymmetric units with anisotropic displacement parameters for every structure are given in the supplementary information. In a couple of the structures there were one or two F atoms that displayed poor thermal parameter shapes (IUCr CheckCIF alert level C). Attempts to model this as disorder added many parameters and decreased the overall quality of the refinement so the disorder was not modeled due to the minor nature. In the structure of $Pr(H_2O)_3(Tf_2N)_3$ the highest difference electron density peaks are not indicative of disorder but are ascribed to the poorer data quality in this case. In the structure of $La(H_2O)_3(Tf_2N)_3·2.5H_2O$, the solvent water molecules were disordered along a channel within the structure. The occupancies were freely refined but thermal parameter restraints were included to keep them all similar. This structure was also found to be twinned and modelled by the twin law 1 0 1 / 0 -1 0 / 0 0 -1 and the scale factor refined to 0.0250(17). This structure also had high residual difference density peak and holes close to the La atoms probably due the twinning. CCDC 1409124-1409133 contains the supplementary crystallographic data for this paper.

For the fully hydrated crystal structures of Gd, Dy, Ho, Er, Yb, Lu and Y bis(trifluoromethylsulfonyl)imides, large unit cells were always obtained and these are listed in Table 2. Example diffraction images for each structure are given in the supplementary information. Although several crystals were tried for each metal, it proved not possible to solve and refine the structures. More discussion is provided in the text.

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Table 1 Pertinent crystallographic and refinement data for $[Sc(H_2O)_7][Tf_2N]_3.H_2O$, $Ce(H_2O)_3(Tf_2N)_3$, $Pr(H_2O)_3(Tf_2N)_3$, $Nd(H_2O)_3(Tf_2N)_3$, $Gd(H_2O)_3(Tf_2N)_3$, $Sm(H_2O)_5(Tf_2N)_3$, $Tb(H_2O)_5(Tf_2N)_3$, $Dy(H_2O)_5(Tf_2N)_3$, $Er(H_2O)_5(Tf_2N)_3$ and $La(H_2O)_3(Tf_2N)_3·2.5H_2O$.

	$[Sc(H_2O)_7][Tf_2N]_3.H_2O$	$Ce(H_2O)_3(Tf_2N)_3$	$Pr(H_2O)_3(Tf_2N)_3$	$Nd(H_2O)_3(Tf_2N)_3$	$Gd(H_2O)_3(Tf_2N)_3$
Empirical formula	$C_6H_{16}F_{18}N_3O_{20}S_6Sc$	$C_6H_6CeF_{18}N_3O_{15}S_6$	$C_6H_6F_{18}N_3O_{15}PrS_6$	$C_6H_6F_{18}N_3NdO_{15}S_6$	$C_6H_6F_{18}GdN_3O_{15}S_6$
Formula weight	1029.54	1034.62	1035.41	1038.74	1051.75
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	cubic	cubic	cubic	cubic
Space group	$P2_1/n$ (no. 14)	$P2_13$ (no. 198)	$P2_13$ (no. 198)	$P2_13$ (no. 198)	$P2_13$ (no. 198)
a/Å	8.8946(4)	18.51715(13)	18.53745(8)	18.4695(2)	18.3973(2)
b/Å	19.9678(10)	18.51715(13)	18.53745(8)	18.4695(2)	18.3973(2)
c/Å	18.7790(8)	18.51715(13)	18.53745(8)	18.4695(2)	18.3973(2)
α/°	90.00	90	90	90	90
β/°	98.166(5)	90	90	90	90
γ/°	90.00	90	90	90	90
Volume/$Å^3$	3301.4(3)	6349.25(7)	6370.16(5)	6300.34(13)	6226.75(12)
Z	4	8	8	8	8
ρ_{calc} / g/cm^3	2.071	2.165	2.159	2.190	2.244
μ/mm^{-1}	0.784	1.996	2.089	2.214	2.703
F(000)	2048.0	3992.0	4000.0	4008.0	4040.0
Crystal size/mm^3	0.12 × 0.12 × 0.06	0.20 × 0.20 × 0.20	0.25 × 0.25 × 0.25	0.40 × 0.30 × 0.20	0.40 × 0.40 × 0.25
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected	17794	9870	35367	17704	35933
Independent	7599 [R_{int} = 0.0211]	4839 [R_{int} = 0.0217]	5355 [R_{int} = 0.0615]	4849 [R_{int} = 0.0587]	5163 [R_{int} = 0.0253]
Data/restraints/ parameters	7599/0/551	4839/6/311	5355/0/296	4849/6/311	5163/6/311
GooF	1.046	1.023	1.185	1.076	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0318, wR_2 = 0.0695	R_1 = 0.0319, wR_2 = 0.0680	R_1 = 0.0519, wR_2 = 0.1233	R_1 = 0.0439, wR_2 = 0.1055	R_1 = 0.0184, wR_2 = 0.0394
Final R indexes [all data]	R_1 = 0.0402, wR_2 = 0.0736	R_1 = 0.0361, wR_2 = 0.0705	R_1 = 0.0542, wR_2 = 0.1244	R_1 = 0.0497, wR_2 = 0.1099	R_1 = 0.0202, wR_2 = 0.0403
Largest diff. peak/hole / e Å^{-3}	0.80/-0.52	0.91/-0.67	1.79/-0.81	1.37/-1.07	0.53/-0.35

	$Sm(H_2O)_5(Tf_2N)_3$	$Tb(H_2O)_5(Tf_2N)_3$	$Dy(H_2O)_5(Tf_2N)_3$	$Er(H_2O)_5(Tf_2N)_3$	$La(H_2O)_3(Tf_2N)_3 \cdot 2.5H_2O$
Empirical formula	$C_6H_{10}F_{18}N_3O_{17}S_6Sm$	$C_6H_{10}F_{18}N_3O_{17}S_6Tb$	$C_6H_{10}DyF_{18}N_3O_{17}S_6$	$C_6H_{10}ErF_{18}N_3O_{17}S_6$	$C_6H_{11}F_{18}LaN_3O_{17.5}S_6$
Formula weight	1080.88	1089.45	1093.03	1097.79	1078.45
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	trigonal
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	P-3 (no. 147)
a/Å	12.9489(3)	12.9085(3)	12.8735(6)	12.8788(4)	15.5598(15)
b/Å	18.4605(5)	18.3690(4)	18.3588(9)	18.2797(7)	15.5598(15)
c/Å	12.9858(3)	12.9307(3)	12.9082(6)	12.8814(5)	8.2562(9)
α/°	90.00	90	90	90	90
β/°	94.507(2)	94.275(2)	94.119(4)	94.524(3)	90
γ/°	90.00	90	90	90	120
Volume/Å^3	3094.56(13)	3057.56(11)	3042.9(2)	3023.10(19)	1731.1(3)
Z	4	4	4	4	2
ρ_{calc} / g/cm^3	2.320	2.367	2.386	2.412	2.069
μ/mm^{-1}	2.482	2.905	3.050	3.375	1.759
F(000)	2092.0	2104.0	2108.0	2116.0	1046.0
Crystal size/mm^3	0.40 × 0.30 × 0.20	0.25 × 0.25 × 0.20	0.20 × 0.20 × 0.15	0.15 × 0.15 × 0.10	0.36 × 0.12 × 0.12
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected	16706	14352	14116	14426	8585
Independent	7124 [R_{int} = 0.0237]	6942 [R_{int} = 0.0184]	6929 [R_{int} = 0.0204]	6912 [R_{int} = 0.0160]	2737 [R_{int} = 0.0352]
Data/restraints/ parameters	7124/15/501	6942/15/501	6929/15/501	6912/15/501	2737/3/164
GooF	1.038	1.017	1.041	1.024	1.187
Final R indexes [I>=2σ (I)]	R_1 = 0.0222, wR_2 = 0.0503	R_1 = 0.0200, wR_2 = 0.0436	R_1 = 0.0222, wR_2 = 0.0485	R_1 = 0.0173, wR_2 = 0.0397	R_1 = 0.0950, wR_2 = 0.2135
Final R indexes [all data]	R_1 = 0.0265, wR_2 = 0.0527	R_1 = 0.0246, wR_2 = 0.0453	R_1 = 0.0267, wR_2 = 0.0510	R_1 = 0.0209, wR_2 = 0.0411	R_1 = 0.0990, wR_2 = 0.2155
Largest diff. peak/hole / e Å^{-3}	0.59/-0.50	0.50/-0.42	0.51/-0.52	0.41/-0.46	4.11/-2.96

Table 2. Unit cell information for the crystal structures of the fully hydrated gadolinium(III), holmium(III), erbium(III), ytterbium(III) and lutetium(III) bis(trifluoromethylsulfonyl)imides. The Z' value is calculated on the basis of a $Ln(H_2O)_8(Tf_2N)_3$ unit having a volume of 972 Å^3 and the Z number of the possible space group (result rounded to nearest integer).

Ln	a/Å	b/Å	c/Å	α/°	β/°	γ/°	V/A^3	Z'	Space group
Gd	26.0571(6)	29.3170(10)	29.7647(9)	89.542(3)	89.781(2)	68.482(3)	21152(1)	11	P-1
Dy	29.6445(6)	30.6765(15)	32.3812(9)	114.941(4)	90.046(2)	90.909(3)	26697(2)	14	P-1
Ho	25.5507(5)	30.5688(4)	54.2424(7)	90	92.2352(14)	90	42334(1)	11	$P2_1/c$
Er	29.7995(10)	30.5975(12)	25.3361(9)	90	113.127(4)	90	21323(1)	11	Pc
Yb	29.8307(9)	30.6068(7)	59.252(3)	90	99.695(5)	90	53326(3)	14	$P2_1/c$
Lu	29.7377(10)	30.6499(10)	59.339(2)	90	99.543(3)	90	53336(3)	14	$P2_1/c$
Y	25.5365(7)	30.6431(13)	54.4861(14)	90	92.209(2)	90	42605(2)	11	$P2_1/c$

Results and Discussion

The hydrated bis(trifluoromethylsulfonyl)imide salts of the trivalent rare earths were synthesised by reaction of the rare-earth oxides with the acid hydrogen bis(trifluoromethylsulfonyl)imide in water. Except in the case of cerium where the stable oxide is CeO_2 so $Ce_2(CO_3)_3$ was used at the starting material.

$$Ln_2O_3 + 6HTf_2N + xH_2O \rightarrow 2Ln(H_2O)_x(Tf_2N)_3 + 3H_2O \quad (1)$$

Initially these reactions were performed under reflux conditions but it was observed that an amount of unreacted acid remained after the reaction. It was found that using a sealed vial of approximately 40 mL in volume for the reactions and heating to 80 °C for one or more hours solved this problem so other syntheses were carried out this way. The rare-earth oxides (or carbonate) were used in excess and remaining solid material filtered from the solution after reaction leaving the metal bis(trifluoromethylsulfonyl)imide salt in an aqueous solution. In order to grow crystals the excess water was removed *in vacuo* on a rotary evaporator and then on a Schlenk line.

The formation and determination of the metal crystals had two major challenges. Firstly, the rate of crystallisation and water evaporation is difficult to control, often resulting in small and badly formed crystals. Additionally, the crystallisation conditions resulted in different structures. That is if the drying was performed at room temperature one crystal type would form and at a higher temperature a second type would form. Secondly, all of the crystals are highly hygroscopic and disappear very quickly when they come into contact with air, often in the period of 5 to 10 seconds. This presents a big challenge in mounting the crystals on the X-ray diffractometer. In order to overcome this, crystals were handled very quickly with a portion of the sample being removed from the sealed vessel and placed on a microscope slide and using a nylon loop, a single crystal very quickly removed and placed in the cold nitrogen gas stream on the X-ray diffractometer.

Due to its smaller size, scandium often behaves differently to Y and the lanthanides and is indeed what we found here. The structure of the crystals was to have scandium coordinated by seven water molecules and with one water of crystallisation in the lattice giving the formula $[Sc(H_2O)_7][Tf_2N]_3{\cdot}H_2O$ (Figure 1). The coordination geometry can be described as distorted monocapped trigonal prismatic[38] with the Sc–O distances varying from 2.1118(15) to 2.1959(14) Å. Each O–H group is involved in intermolecular hydrogen-bonds to other O or N atoms making a complex three-dimensional structure.

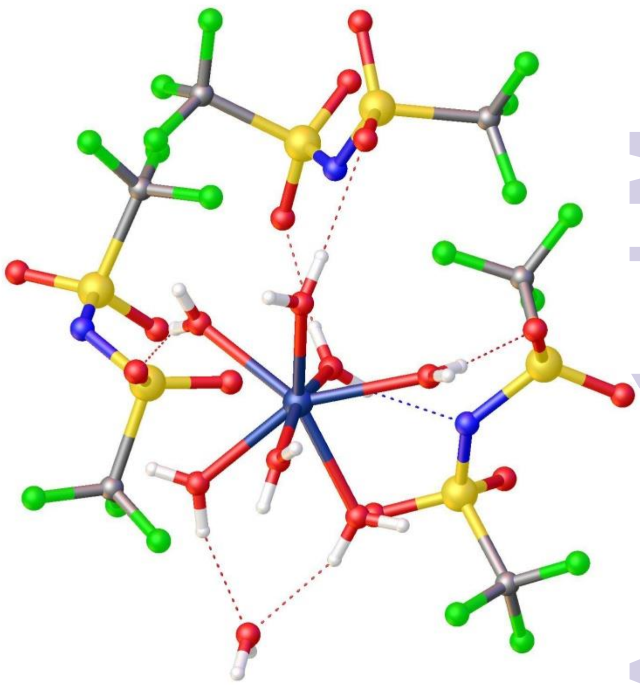

Figure 1. View of the crystal structure of $[Sc(H_2O)_7][Tf_2N]_3{\cdot}H_2O$.

There is a high degree of variability of hydration number in scandium(III) hydrate crystal structures. Seven coordination has been seen in $[Sc(H_2O)_7][Tf_3C]_3.H_2O$ (Tf_3C = tris(trifluoromethylsulfonyl)methide) and here there is also a water of crystallisation.[39] The Sc-O distance in $[Sc(H_2O)_7][Tf_3C]_3{\cdot}H_2O$ are 2.113–2.222 Å, so similar to $[Sc(H_2O)_7][Tf_2N]_3{\cdot}H_2O$. In $[Sc(H_2O)_8][TfO]_3$ (TfO = trifluoromethanesulfonate) the scandium is eight-coordina and there are no waters of crystallisation.[37] In the eigh coordinate structure the distances are seven Sc-O distances of a similar length (2.146–2.291 Å) and one slightly longer (Sc-O = 2.536 Å). Six coordinate scandium has been seen in $[Sc(H_2O)_6][Sc(OMs)_6]$ (OMs = methanesulfonate).[40] In the six coordinate structure, the Sc-O distances (2.085 Å) are slightly shorter than in $[Sc(H_2O)_7][Tf_2N]_3{\cdot}H_2O$.

Due to ionic radius of Y^{3+}, it is frequently behaving chemically similar to the heavy lanthanides. In this study, the results group yttrium with the heavy lanthanides and so yttrium will be considered a part of the heavy lanthanides for this discussion.

There were three main structural types found for the lanthanide series. The early lanthanides La–Gd (except Sm were found to crystallise with structure $Ln(H_2O)_3(Tf_2N)_3$, where the Ln(III) ion is coordinated by three water molecules and three bidentate Tf_2N anions giving a total coordination number of nine (Figure 2). This structure has previously been reported for La and Nd.[33,34] For the elements Ce, Pr, and Nd this structure was found when the compounds were crystallised at room temperature. For the heavier rare-earth Gd, the structure only formed at higher temperatures.

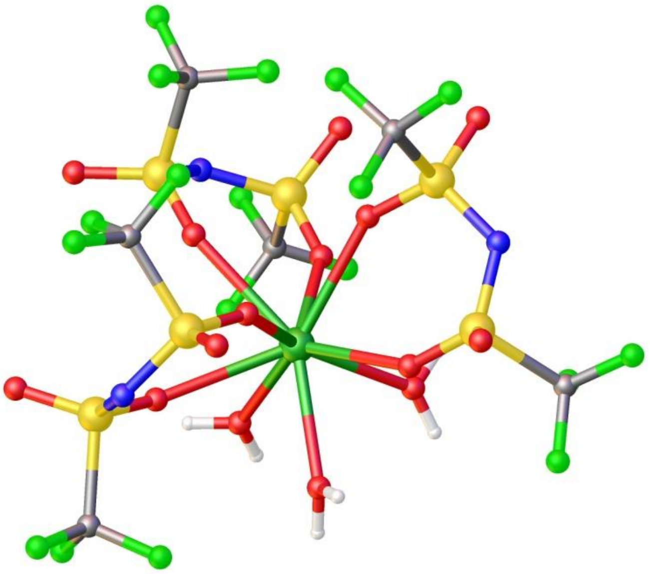

Figure 2. View of the crystal structure of $Ce(H_2O)_3(Tf_2N)_3$.

There are two crystallographically independent $Ln(H_2O)_3(Tf_2N)_3$ molecules in the asymmetric unit and both these $Ln(H_2O)_3(Tf_2N)_3$ molecules are located on a three-fold rotation axis. This means that the independent unit consists of one third of a Ln centre, one water molecule and one bis(trifluoromethylsulfonyl)imide anion two times. There are only three crystallographically independent Ln–O distances per molecule. The Ln–O bond distances to the water molecules are shorter than those to the Tf_2N anions. The Ln–O bond lengths decrease in length with decreasing ionic radius of the Ln^{3+} ion along the series Ce Pr, Nd and Gd as expected (Table 3), although the overall volume of the unit cells do not show this decreasing trend. The unit cell for Pr is slightly larger than that of Ce (Table 1) which must be due to small differences in intermolecular interactions as the ionic radius is indeed smaller.

Table 3. Ln–O bond distances within the crystal structures $Ln(H_2O)_3(Tf_2N)_3$ (Ln = Ce, Pr, Nd, Gd). There are two symmetry independent molecules in each structure, which are listed separately.

	Ln–O(water) / Å	Ln–O(Tf$_2$N) / Å
$Ce(H_2O)_3(Tf_2N)_3$ 1	2.454(3)	2.519(3), 2.529(3)
$Ce(H_2O)_3(Tf_2N)_3$ 2	2.455(3)	2.517(3), 2.547(3)
$Pr(H_2O)_3(Tf_2N)_3$ 1	2.451(5)	2.512(5), 2.524(6)
$Pr(H_2O)_3(Tf_2N)_3$ 2	2.438(6)	2.504(5), 2.548(5)
$Nd(H_2O)_3(Tf_2N)_3$ 1	2.421(4)	2.482(4), 2.499(4)
$Nd(H_2O)_3(Tf_2N)_3$ 2	2.417(4)	2.483(4), 2.521(4)
$Gd(H_2O)_3(Tf_2N)_3$ 1	2.3637(18)	2.4404(17), 2.4697(17)
$Gd(H_2O)_3(Tf_2N)_3$ 2	2.3654(17)	2.4272(17), 2.4924(17)

The middle and heavy lanthanides were found to have the crystal structure $Ln(H_2O)_5(Tf_2N)_3$, where the Ln is coordinated by five water molecules and three monodentate Tf_2N anions giving a total coordination number of eight (Figure 3). For the case of Sm, these crystals formed at room temperature but for Tb, Dy and Er, high temperatures were required for formation. This structure has also been reported for Yb with the crystals synthesised from anhydrous $Yb(Tf_2N)_3$ in *p*-xylene solution with a small amount of water and heptanoic acid added.[34]

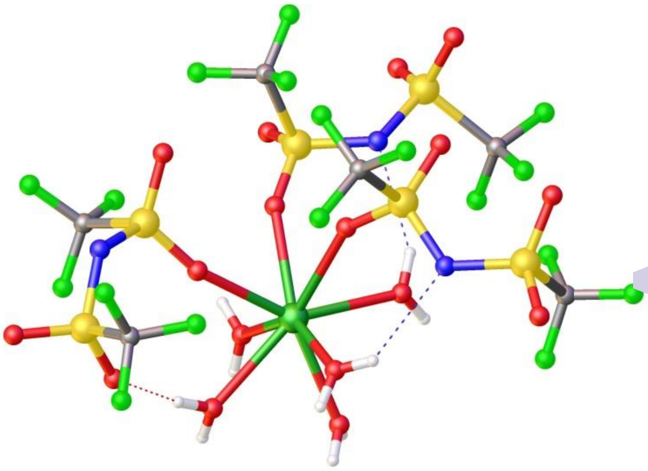

Figure 3. View of the crystal structure of $Sm(H_2O)_5(Tf_2N)_3$.

Table 4. Ln–O bond distances within the crystal structures $Ln(H_2O)_5(Tf_2N)_3$ (Ln = Sm, Tb, Dy, Er).

	Ln–O(water) / Å	Ln–O(Tf_2N) / Å
$Sm(H_2O)_5(Tf_2N)_3$	2.3552(17) 2.3776(18) 2.3906(16) 2.4012(16) 2.4045(16)	2.4113(16) 2.4341(15) 2.4572(15)
Average	2.386	2.434
$Tb(H_2O)_5(Tf_2N)_3$	2.3198(16) 2.3319(16) 2.3524(16) 2.3598(16) 2.3701(16)	2.3697(15) 2.4023(16) 2.4289(15)
Average	2.347	2.400
$Dy(H_2O)_5(Tf_2N)_3$	2.2997(18) 2.3202(18) 2.3425(18) 2.3431(17) 2.3597(17)	2.3542(17) 2.3950(16) 2.4240(16)
Average	2.333	2.391
$Er(H_2O)_5(Tf_2N)_3$	2.2814(15) 2.2943(15) 2.3198(14) 2.3286(14) 2.3381(14)	2.3684(13) 2.3997(14) 2.3447(14)
Average	2.312	2.371

Like in the structures of $Ln(H_2O)_3(Tf_2N)_3$, the Ln–O bond distances to the water molecules are shorter than those to the Tf_2N anions (Table 4). Also the lanthanide contraction can be seen with the later lanthanides having, on average, shorter bond distances.

The final structural type was found for the late lanthanides Gd-Lu (except Tm) and contains the Ln fully coordinated by water molecules and no coordinated bis(trifluoromethylsulfonyl)imide anions. Unfortunately in every case the resulting crystal structures were highly disordered and a full structural refinement was never possible. There are several complicating factors that contribute to the problems of solving and refining the structures. The crystals are small and due to their hygroscopic nature, they decrease in size on attempting to mount on the X-ray diffractometer. The structures have very large unit cells and hence this means that there are a lot crystallographically independent cations and anions in the crystallographic asymmetric unit (Table 2) meaning that the structures are difficult to solve and refine. The Z' value was calculated based on the possible space group symmetry and the fact that each non-hydrogen atom will occupy approximately 18 $Å^3$,[41] and so each $[Ln(H_2O)_x][Tf_2N]_3$ will contain 54 non-hydrogen atoms (assuming x = 8) and have a volume of 978 $Å^3$. Of course, this does not take into account the possibility of solvent waters in the lattice. Also due to the large unit cells and disorder, the diffraction falls off with 2-theta fairly quickly and, thus, the high angle data are poor. In the unit cells of Gd and Dy, there are two angles close to but not equal to 90°, this is close to being monoclinic so can cause pseudo-symmetry effects. In the case of Ho, Yb and Y, where it is monoclinic, the space group was difficult to determine.

Several attempts were made to collect data on these crystals and in the best case of $[Er(H_2O)_x][Tf_2N]_3$ it was possible to partially solve the structure in space group *Pc* and find the heavy atom positions of 10 Er centres, all which had a number of oxygen atoms at reasonable distances from the Er centre. It was not clear enough to definitively determine the coordination number of the Er centres, however in the Cambridge Structural Database there are either $[Er(H_2O)_8]^{3+}$ and $[Er(H_2O)_9]^{3+}$ cations depending on the structure.[42] In addition 44 sulphur atom positions could be detected – three quarters of the required 60 to match 10 Er^{3+} cations. It was also possible to identify two whole Tf_2N anion and several partial ones – e.g. the nitrogen atom between two sulphur atoms or oxygen atoms attached to the sulphur atoms. With part of the structure refined the R1 value was, at best 17%, so nowhere near publishable quality but it was possible to determine that the structure contained discrete Er centres and bis(trifluoromethylsulfonyl)imide anions, these Er centres were fully coordinated by water molecules and the bis(trifluoromethylsulfonyl)imide anions were very disordered. Despite our best efforts, for the other elements it was not even possible to obtain the heavy atom positions in the structure. However, similarities can be seen between the six unit cells (Table 2). They all have a Z' of 11 or 14. Ho and Y have very similar unit cells, and both of these are exactly twice the size of Er and Gd. Yb and Lu also have very similar unit cells and they are twice the size of Dy.

In the case of Tm, we were unable to isolate any single crystals except on one occasion very small crystals were obtained, which turned out to have a monoclinic *I* centred unit cell with dimensions a=26.932(2) Å, b=12.9484(8) Å, c=29.030(3) Å, β = 109.819(11)°, V = 9524.1(16) $Å^3$. Although the data quality was poor, the structure could be solved and refined to have formula $[Tm_6(O)(OH)_8(OH_2)_{16}(Tf_2N)_2][Tf_2N]_6\cdot xH_2O$. The best final R1 value obtained was 11.5% but the final difference electron density had unexplainable features so the data are not good enough to publish the structure.

For the case of $La(H_2O)_3(Tf_2N)_3$ a second crystal type of crystal could be isolated, which had a hexagonal symmetry and some additional water molecules within the crystal lattice and the overall formula $La(H_2O)_3(Tf_2N)_3\cdot 2.5H_2O$. The coordination around the La centre of three waters and three bidentate bis(trifluoromethylsulfonyl)imide anions was the same as the cubic structure discussed above. However, in the hexagonal structure the packing formed a channelled structure containing some highly disordered water molecules (Figure 4). This same structure was reported for Ln = Eu by Kawamura *et al*.[34] In that paper, the authors suggest that the templating effect of *n*-heptanoic acid was required to form the hexagonal crystals and that the molecules within the channels were dodecane,[34] however in our system we did not have organic molecules of any kind present. One thing that was different in the samples that contained $La(H_2O)_3(Tf_2N)_3\cdot 2.5H_2O$ was that there was a small excess of HTf_2N left over from the synthesis (as determined by universal indicator paper) so this could have somehow provided a templating effect.

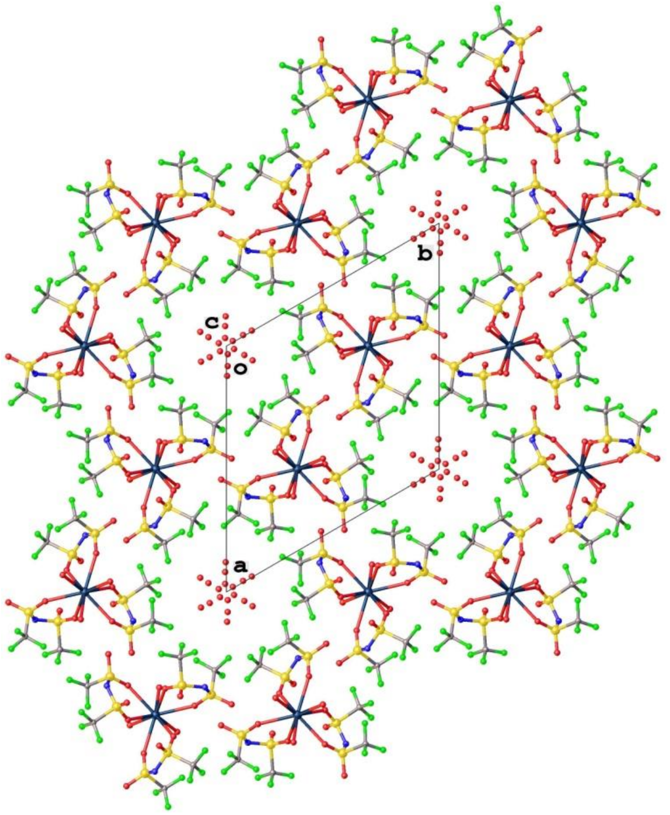

Figure 4. View of the packing in the crystal structure of $La(H_2O)_3(Tf_2N)_3\cdot2.5H_2O$ showing the disordered water molecules.

Conclusions

Most of the lighter lanthanides crystallised during the drying process on the Schlenk line at room temperature giving the structure with three coordinated waters and three bidentate Tf_2N anions. Lower pressures and longer heating times were necessary for the heavier lanthanides in order to remove all the water and to form crystals of the fully hydrated metal salts. The crystallisation temperature has a big influence on the crystal structure: the heavy rare earths (Ln = Gd, Dy, Ho, Er, Yb, Lu and Y) crystallised with a fully hydrated coordination sphere when a drying procedure was applied at room temperature. The strangely large unit cells of these fully hydrated heavy rare-earth structures prevented full structural characterisation. Crystallisation at a higher temperature (60 °C) gave structures for Ln = Tb, Dy, Er and Yb with only five coordinated water molecules, whilst for Ln = Gd this gave the structure with three coordinated water molecules.

The lighter lanthanides have a low affinity for water preferring to coordinate to the Tf_2N anions in a bidentate fashion. In the middle of the series there is a switch of the Tf_2N anion coordination from bidentate to monodentate so the number of water molecules coordinating increases. The heavier lanthanides have a high affinity for water and prefer to coordinate water over the Tf_2N anions.

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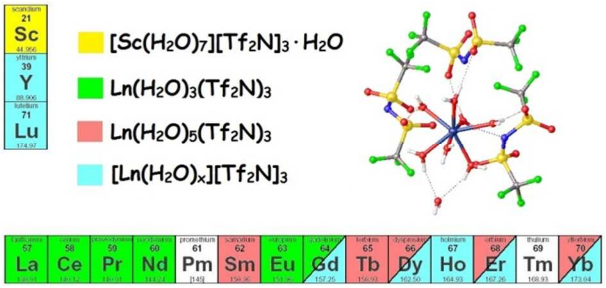

Structural characterisation of the full range of hydrated rare-earth bis(trifluoromethylsulfonyl)imide salts showed the structures to be $[Sc(H_2O)_7][Tf_2N]_3 \cdot H_2O$, $Ln(H_2O)_3(Tf_2N)_3$, $Ln(H_2O)_3(Tf_2N)_3$ or $[Ln(H_2O)_x][Tf_2N]_3$.