Structural versatility in hydrated rare earth(III) 1,2-benzenedisulfonates†

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The complexes $Ln_2L_3 \cdot xH_2O$ (L = 1,2-benzenedisulfonate; Ln = Sc (**1**), x = 14; Ln = Y (**2**), x = 16; Ln = La (**3**), x = 7; Ln = Ce (**4**), x = 6; Ln = Pr (**5**), x = 10; Ln = Nd (**6**), x = 18; Ln = Sm (**7**), x = 18.25; Ln = Eu (**8**), Gd (**9**), Tb (**10**), Ho (**11**), Yb (**12**), Lu (**13**), all x = 16) were synthesised by treating Ln_2O_3 with an aqueous solution of 1,2-benzenedisulfonic acid. Single crystal X-ray studies revealed isomorphous structures of the type, $[LnL(H_2O)_6]_2[L] \cdot 4H_2O$ for **2**, **8–13**, *i.e.* Ln = Eu–Lu (including Y) and, presumptively, intermediate Ln. These contain eight-coordinate Ln with the disulfonate ligand coordinating though one oxygen of each sulfonate group giving a seven-membered chelate ring. Complexes of the 'earlier' Ln are less systematically defined. The samarium complex, **7**, is so far unique, with the structure $[SmL(H_2O)_6][SmL_2(H_2O)_4] \cdot 8\frac{1}{4}H_2O$. There is an eight-coordinate complex anion with two cisoid chelating disulfonate ligands (again seven-membered rings), and four unidentate water molecules, and an eight-coordinate cation, which is similar to those of **2**, **8–13**. A novel lanthanum complex $[H_7O_3][LaL_2]$ (**14**) has been prepared by the treatment of La_2O_3 with an excess of aqueous 1,2-benzenedisulfonic acid and by treatment of **3** with perfluoroadipic acid in water. The complex anion forms polymeric chains with eight-coordinate lanthanum ions and μ-η^2(O,O′):η^2(O″,O‴)-disulfonate groups. Two oxygen atoms from each sulfonate group (O, O″ from one; O′, O‴ from the other) bridge pairs of adjacent La ions. In addition O, O′ (and O″, O‴) form seven-membered chelate rings with neighbouring lanthanum atoms. Two uncoordinated oxygen atoms of each dianion are hydrogen bonded to the $H_7O_3^+$ ions. Another cationic lanthanum complex, $[LaL(H_2O)_7]Cl \cdot H_2O$ (**15**), from attempts to crystallize $[La_2L_3] \cdot 7H_2O$, has a nine-coordinate La ion with a chelating disulfonate ligand and seven unidentate water molecules, and may provide some insight into the possible structures of complexes **3–6**. In all structures, hydrogen-bonding involving water of crystallization links the cations and the anions in a supramolecular superstructure.

Introduction

Sulfonate ions RSO_3^- are excellent leaving groups in organic syntheses[1] and are readily displaced by ligands or counter ions in inorganic syntheses.[2] With oxophilic lanthanoid ions, lanthanoid triflates are effective catalysts,[3] *e.g.* in Friedel-Crafts reactions.[4,5] Coordination of triflate to lanthanoids is sufficiently strong to thwart complete displacement on attempts to use them in metathesis reactions[6–11] as an alternative to trihalides.[12] However, in aqueous solution, coordination by water competes with sulfonate ligation, and tosylate ions give $[Ln(O_3SR)_2(H_2O)_6](O_3SR) \cdot 3H_2O$ (R = p-MeC_6H_4) complexes for Ln = Y, Sm–Lu, but cannot compete with water for the larger lanthanoids where $[Ln(H_2O)_9][RSO_3]_3$ (Ln = La, Ce, Nd) species are isolated.[13] The formally chelating 1,2-benzenedisulfonate ion (L^{2-}) should compete better with water and has the potential to be a polyfunctional ligand, especially in view of the role of dicarboxylates in crystal engineering.[14] However, there are only some alkali metal derivatives[15] and one nickel complex[16] with reported structures, apart from our initial study of some heterobimetallic lanthanoid complexes.[17,18] Attempts to crystallize Ln_2L_3 species from solutions of lanthanoid oxides in aqueous 1,2-benzenedisulfonic acid (eqn (1)) initially gave bimetallic complexes $[KLnL_2]$ owing to leakage of K^+ from an ion exchange column. These bimetallic compounds were then obtained by deliberate syntheses (eqn (2) and (3)).[17,18] The structures of $[K(H_2O)_2LnL_2]$ (Ln = La or Nd), which are polymeric networks with lanthanoid sulfonate chains crosslinked though coordination to potassium, and of $[K(H_2O)Yb(H_2O)_4L_2]$, a tetranuclear heterobimetallic array, offered evidence of the coordination versatility of the 1,2-benzenedisulfonate ligand. The bulk products (Ln_2L_3) of the initial syntheses after drying at 160–200 °C, were obtained as fractional ethanol solvates of unknown structure,[17,18] a form unsuitable for crystallographic investigation. Because of the proven value of these reagents in the synthesis of bimetallic networks and their capacity for a range of binding modes[17,18] we have pursued crystallization of

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the original Ln_2L_3 target complexes for a range of lanthanoid elements, and report the syntheses of Ln_2L_3 hydrates, together with the crystal structures of representative compounds for Ln = Sm–Lu. Although single crystals of Ln_2L_3 hydrates could not be obtained for the lighter lanthanoids, we also report the synthesis and structure of $[H_7O_3][LaL_2]$ and the structure of $[LaL(H_2O)_7]Cl\cdot H_2O$. Unexpectedly, the bulk of these complexes contain mononuclear species rather than form polymers or networks, and they have considerable unused donor capacity which can potentially be used in the synthesis of bimetallic networks.

$$Ln_2O_3 + 3H_2L \rightarrow [Ln_2L_3] + 3H_2O \qquad (1)$$

$$[Ln_2L_3] + K_2L + 4H_2O \rightarrow 2[K(H_2O)_2LnL_2] \quad (Ln = La \text{ and } Nd) \qquad (2)$$

$$[Yb_2L_3] + K_2L + 10H_2O \xrightarrow{EtOH} 2[K(H_2O)Yb(H_2O)_4L_2] \qquad (3)$$

Results and discussion

Syntheses

Rare earth(III) 1,2-benzenedisulfonate complexes were synthesised by heating an excess of Ln_2O_3 with 1,2-benzenedisulfonic acid (H_2L) in water at reflux (eqn (1)). Subsequent work-up of the mixture by filtration and evaporation of the water afforded $Ln_2L_3\cdot xH_2O$, **1–13** (L = 1,2-benzenedisulfonate; Ln = Sc (**1**), x = 14; Ln = Y (**2**), x = 16; Ln = La (**3**), x = 7; Ln = Ce (**4**), x = 6; Ln = Pr (**5**), x = 10; Ln = Nd (**6**), x = 18; Ln = Sm (**7**), x = 18.25; Ln = Eu (**8**), Gd (**9**), Tb (**10**), Ho (**11**), Yb (**12**), Lu (**13**), all x = 16). Single crystals of the complexes **2**, **7–13** were obtained by concentration of the solutions until they became viscous and then leaving them to stand until crystallization occurred. Attempts to obtain single crystals of **1**, **3–6**, from aqueous and aqueous ethanol solutions, afforded fine needles, unsuitable for X-ray studies, suggesting that they crystallize with different forms and structures. However, two lanthanum complexes were obtained that were amenable to crystallographic characterization, *viz*. $[H_7O_3][LaL_2]$ **14** and $[LaL(H_2O)_7]Cl\cdot H_2O$ **15**. The former was obtained in high yield from the reaction of lanthanum oxide with an excess of the disulfonic acid in water (eqn (4)). It was also obtained from an unsuccessful attempt to make a mixed ligand complex by reaction of La_2L_3 with perfluoroadipic acid, with the fluorinated acid acting simply as a proton source (eqn (5)). The chloride complex (**15**) resulted fortuitously due to trace chloride contamination in an attempt to crystallize $[La_2L_3]$ from an aqueous solution and was not representative of the bulk material.

$$[La_2L_3] + 6H_2O + H_2L \rightarrow 2[H_7O_3][LaL_2](\mathbf{14}) \qquad (4)$$

$$[La_2L_3] + 3H_2O + H^+ \longrightarrow [H_7O_3][LaL_2](\mathbf{14}) + LaL^+ \qquad (5)$$

Although microanalyses and metal analyses for complexes **2**, **12–14** agree with the compositions shown by the X-ray crystal structures, the data for bulk samples of $[Ln_2L_3]\cdot xH_2O$ compounds **7–11** are indicative of lower water content than determined by X-ray crystallography, consistent with ready efflorescence. Similarly, the compositions for bulk **1**, **3–6** (x = 6–14) may be indicative of less water of crystallization than when freshly isolated. The preparation of **3**, **6** and **12** as hydrates contrasts with the previous isolation of anhydrous lanthanum, neodymium and ytterbium 1,2-benzenedisulfonates containing a trace of ethanol.[18] All infrared spectra showed multiple absorptions attributable to ν(SO) vibrations, and either a very broad ν(OH) band or, for **2**, **12**, **13** a multiple feature broad absorption. The visible/near IR spectra of the Pr, Sm, Nd, Ho and Yb complexes showed the expected features for the appropriate Ln^{3+} ions (see Experimental).[19] The negative electrospray mass spectra of all complexes in methanol showed the LnL_2^- ion, with often solvated variants, *e.g.* $LnL_2(MeOH)^-$, despite the fact that no structurally characterized complex apart from $[SmL(H_2O)_6][SmL_2(H_2O)_4]$ **7** has been shown to contain a mononuclear LnL_2^- ion. (In addition, crystalline $[H_7O_3]^+[LaL_2]^-$ **14** contains a polymeric $(LaL_2^-)_n$ chain). Only **3**, **4**, **9** and **14** gave positive electrospray mass spectra, with all showing a LnL^+ ion and, also, solvated analogues. Although **9** and plausibly **3** and **4** contain a hydrated LnL^+ complex, **14** does not. Thus, some partial ionic rearrangement occurs in the very dilute solutions used for ESMS.

$$\text{“}Ln_2L_3\text{”} \leftrightarrow LnL^+ + LnL_2^-$$

$$[H_7O_3][LaL_2] \leftrightarrow LaL^+ + L^{2-} + H_3O^+ + 2H_2O$$

The molar conductivities of $\sim 10^{-3}$ M solutions of $[SmL(H_2O)_6][SmL_2(H_2O)_4]$ (**7**) and $[HoL(H_2O)_6]_2L$ (**11**), two complexes with different solid state compositions (below), were similar in both water and methanol. In the former, very high values ($\sim$400 S cm^2 mol^{-1}) indicate extensive dissociation into component Ln^{3+} and L^{2-} ions, driven by the coordination of water at low concentrations. The values in methanol are below the range for a 1 : 1 electrolyte[20] for both the (solid state) 1 : 1 electrolyte (**7**) and the 2 : 1 (**11**), indicative of extensive ion pairing in these solutions and providing a basis for the ionic redistributions observed by ESMS. In the ^1H NMR spectra of the complexes in D_2O, the aromatic resonances of the Sm and Eu complexes are little shifted from the values for diamagnetic **1–3**, **13**, **14**. Those of Ce and Nd complexes move 0.2–0.3 ppm to lower frequencies and **5** (Pr) somewhat more ($\sim$0.6 ppm), whereas the chemical shifts of the terbium and ytterbium complexes move 0.5–0.9 ppm to higher frequencies. The relatively small shifts for the paramagnetic complexes also suggest substantial dissociation in aqueous solution with coordinated L displaced by water.

Single crystal X-ray studies

X-Ray crystal structure determinations have been carried out for the 1,2-benzenedisulfonate complexes **2**, **7**, **8**, **10–13**, **14** and **15**. In addition, the unit cell dimensions of **9** were determined and found to be similar to those of **2**, **8** and **10–13**. Attempts to encompass the full range of rare earth ion sizes, including Sc, to determine the effect of the ionic radius on the structure have been frustrated by a lack of suitable crystals of **1**, **3–6**. A structure has been determined for the yttrium complex **2**, this element behaving chemically and structurally as a heavy rare earth because of the size of its ionic radius.[21]

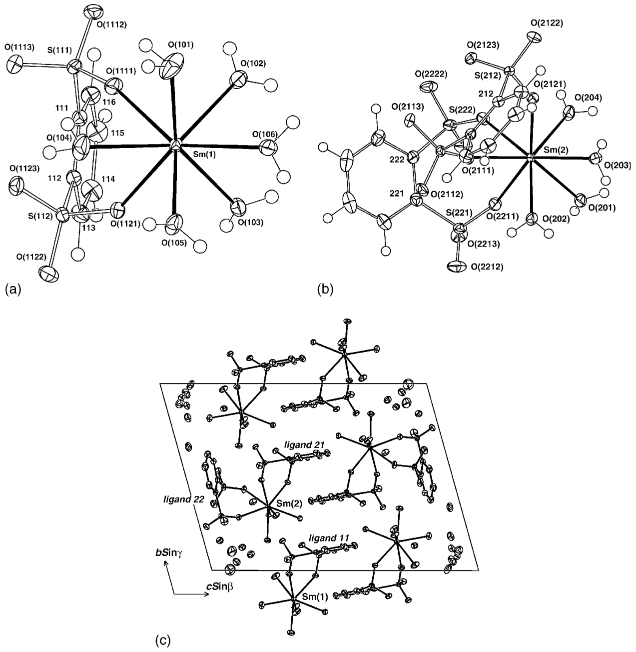

Fig. 1 (a,b) The cation and anion of $[SmL(H_2O)_6][SmL_2(H_2O)_4]\cdot$'$8\frac{1}{4}H_2O$' (**7**), projected down the quasi-$\bar{4}$ axes of their (approximately) square-antiprismatic coordination environments. (c) The unit cell contents, projected down *a*, showing the interleaving and inverse packing relationship of the aromatic planes of the ionic components of the lattice array.

$[Sm(C_6H_4(SO_2\cdot O)_2)(H_2O)_6][Sm(C_6H_4(SO_2\cdot O)_2)_2(H_2O)_4]\cdot$'$8\frac{1}{4}H_2O$' (7). The results of the low temperature X-ray crystal structure determination of complex **7** are consistent in terms of stoichiometry and connectivity with an ionic coordination compound containing discrete mononuclear complex cation–anion pairs (Fig. 1a, b), modelled as solvated with water molecule fragments. One formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. The cationic samarium component is eight-coordinate (two Sm–$O_{sulfonate}$ and six Sm–O_{water} bonds) with a chelating sulfonate ligand bonded though one oxygen atom of each SO_3 group. The anionic samarium component is also eight-coordinate, but in this case, two cisoid disulfonate ligands form η^2-chelates to the metal centre, again, with one oxygen atom from each SO_3 group bonded. The chelating ligands form seven-membered rings in both the cationic and anionic complexes. Such seven-membered chelate rings have been previously observed for the 1,2-benzenedisulfonate ligand in $[K(H_2O)YbL_2(H_2O)_2]$[18] and with the much smaller Ni^{2+} ion.[15] By contrast, the bimetallics $[K(H_2O)LnL_2]$ (Ln = La, Nd) have only bridging disulfonate groups.[18] The overall polyhedra of the donor atoms around the samarium metal centres are quasi-square antiprismatic[22] for both Sm(1) and Sm(2) (Fig. 1; Table 1). The Sm–$O_{sulfonate}$ bond distances (av. Sm(1) 2.404(3), Sm(2) 2.39(2) Å) are close to those of Sm–O_{water} (av. Sm(1) 2.42(3), Sm(2) 2.42(4) Å) (Table 1) in both the cationic and anionic units. The range of Sm–O_{water} distances is similar in the cation and the anion. Values of bond lengths for Sm–O_{water} and Sm–$O_{sulfonate}$ are consistent with values reported for other such (eight-coordinate) distances.[13,23–25] Subtraction of the ionic radius for eight

Table 1 The samarium environments in **$[SmL(H_2O)_6][SmL_2(H_2O)_4]\cdot$'$8\frac{1}{4}H_2O$'** (**7**), *r* is the metal–donor atom distance; the other entries in the matrices are the angles (degrees) subtended by the atoms at the head of the relevant row and column.

(a) The $[SmL(H_2O)_6]^+$ cation: the Sm(1) environment.[a]

Atom	r/Å	O(1121)	O(101)	O(102)	O(103)	O(104)	O(105)	O(106)
O(1111)	2.406(1)	73.61(4)	83.85(6)	73.82(5)	112.73(5)	74.18(6)	141.72(5)	143.64(6)
O(1121)	2.402(1)	—	143.38(5)	117.45(5)	70.60(4)	74.23(5)	81.30(5)	137.02(5)
O(101)	2.376(2)	—	—	81.90(6)	145.90(5)	72.02(6)	100.82(7)	76.28(1)
O(102)	2.428(1)	—	—	—	75.16(5)	140.39(6)	144.38(5)	73.46(5)
O(103)	2.436(2)	—	—	—	—	139.80(5)	84.47(6)	73.23(5)
O(104	2.459(2)	—	—	—	—	—	71.42(6)	125.74(6)
O(105)	2.385(2)	—	—	—	—	—	—	72.81(5)
O(106)	2.418(1)	—	—	—	—	—	—	—

(b) The $[SmL_2(H_2O)_4]^-$ anion: the Sm(2) environment[b]

Atom	r/Å	O(2121)	O(2211)	O(2221)	O(201)	O(202)	O(203)	O(204)
O(2111)	2.388(1)	74.29(4)	83.95(5)	74.50(5)	144.83(4)	73.91(5)	118.42(5)	138.95(5)
O(2121)	2.366(1)	—	151.25(5)	83.95(4)	136.46(5)	111.67(5)	72.45(4)	78.99(5)
O(2211)	2.400(1)	—	—	72.10(4)	70.86(5)	79.02(5)	135.68(4)	107.43(5)
O(2221)	2.411(2)	—	—	—	117.95(5)	138.88(5)	147.27(4)	72.17(1)
O(201)	2.453(1)	—	—	—	—	77.40(5)	70.25(5)	73.85(5)
O(202)	2.417(1)	—	—	—	—	—	72.54(5)	146.15(6)
O(203)	2.457(2)	—	—	—	—	—	—	81.13(6)
O(204)	2.370(2)	—	—	—	—	—	—	—

[a] Sm(1)–O(1111,1121)–S(111,112) are 162.29(9), 142.89(8)°; Sm(1) lies 2.902(4) Å out of the associated C_6 aromatic plane. The C_6(Ar)/O(4) (associated square face of the coordination environment) interplanar dihedral angles are 71.28(6), 25.98(6) (ligands 21,22). [b] Sm(2)–O(2111,2121; 2211,2221)–S(211,212; 221,222) are 159.23(9), 145.47(9); 154.77(9), 139.73(7)°; Sm(2) lies 2.975(4), 2.986(4) Å out of the associated C_6 planes. The C_6/O(102,103,1111,1131) interplanar dihedral angle is 80.41(6)°.

coordinate Sm^{3+} from the average Sm–O distances gives values of 1.31–1.34 Å, consistent with those for $[K(H_2O)_2NdL_2]_n$.[18]

The packing diagram (Fig. 1c) shows hydrophilic regions of oxygen-coordinated lanthanoid cations and separate hydrophilic water of crystallization layers, alternating with hydrophobic regions of aromatic moieties stacked parallel to *b*, the stacking mode representing an energetically favourable arrangement of aromatic groups.[26–28] One phenyl ring of the anionic complex and the ring of the cation interleave, the other of ligand 2 confronting its inversion image. Strong hydrogen-bonding links anion and cation components through the intermediary lattice water molecule 01: O(01)··· H(202a) (x, $y - 1$, z), H(204a) ($x - 1$, $y - 1$, z), both *ca.* 1.9 Å, with H(01a)···O(2112) (x, $y - 1$, z), H(01b)···O(2212) (x, $y - 1$, z) both *ca.* 2.0 Å. The hydrogen atoms of water molecule 02 link sulfonate oxygens of different anions (H(02a)···O(2222) ($x - 1$, $y - 1$, z) *ca.* 1.95 Å; H(02b)···O(2223) ($2 - x$, $\bar{y}$, $\bar{z}$) *ca.* 1.8 Å). Beyond these, the hydrogen-bonding is more diffuse. The remainder of the hydrogen atoms of the majority of the coordinated and well-defined lattice water molecules, connect, only one from each pair, with an oxygen atom of a well-defined anion or water molecule. The remainder interact with the disordered regions about the *a* axis. The overall estimate of the degree of hydration is tentative; the disordered component of the array ('$5\frac{1}{4}$ H_2O') is readily lost, as is evident from the analytical composition for the bulk product. It is plausible that this structural form extends to larger lanthanoids, as the complexes of the smaller lanthanoids, even the adjacent Eu, have a different structure. Attempts to probe structures of complexes of the larger lanthanoids by X-ray powder photography were frustrated by ready efflorescence (see *e.g.* the differing hydration of bulk **3–6**). The strong H-bonding links between the cation and the anion provide a basis for the ion pairing observed in dilute solutions in methanol.

$[Ln(C_6H_4(SO_2 \cdot O)_2)(H_2O)_6]_2[C_6H_4(SO_3)_2] \cdot 4H_2O$, Ln = Y, Eu, Tb, Ho, Yb, Lu (2, 8, 10, 11, 12, 13). These complexes are isomorphous, defining a 'domain of existence' for the heavy rare earths from Ln = Eu onwards, including Y, presumptively accessible for other intermediate members, as indicated by unit cell data for **9** (Ln = Gd). The results of the single crystal X-ray structure determinations are consistent with their formulation as ionic arrays with complex $[LnL(H_2O)_6]^+$ cations (similar to that found in **7**) (Fig. 2(a), Table 2) and L-counterions, solvated by well-defined water molecules. The hydrogen atoms of the latter were confirmed by refinement for the Ln = Eu example, **8**, with difference map evidence consistent with that model for the remainder. One half of the formula unit comprises the asymmetric unit of the structure, containing one cation, devoid of crystallographic symmetry, one-half of the anion which lies with the Ln atom in the crystallographic mirror plane, and two water molecules. Geometries are compared for the ligand component of the cation and the anion for the most precisely described systems, those for Ln = Y, Lu in Table 3, showing that, despite the wide divergences observed in Ln–O–S angles (Table 1 and 2), coordination, presumably largely 'ionic' in nature, has little impact on the L geometry, with S–O distances and O–S–O angles differing little between coordinated and free L (Table 3). Consistent between the latter and of interest are the large differences in exocyclic angles at each pendant sulfur and the lengthened distance between the substituted carbon atoms. The variation in Ln–O distances between Ln = Eu, Lu (size extremes) is in accord with expectations from the lanthanoid contraction and consistent with the reduction in Ln^{3+} radius of *ca.* 0.09 Å.[21] Likewise, data for Ln = Y conform to ion size predictions (Table 2). The Ln–O bond distances are also similar to those of the related $[Ln(O_3SR)_2(H_2O)_6](O_3SR) \cdot 3H_2O$ (R = *p*-MeC_6H_4, Ln = Y, Sm, Gd, Dy, Ho, Er, Yb, Lu;[13] R = $O_3SC_{10}H_7$-2, Ln = Y, Pr, Eu, Gd, Dy, Er, Yb[24,25]). However, the similarities end there, as the RSO_3 ligands are transoid (O–Ln–O *ca.* 140°)[13,24,25] whereas the disulfonate *O*-donors are necessarily cisoid (O–Ln–O *ca.* 73°) (Table 2), the bite angles increasing with decrease in Ln^{3+} radius. Further, the disulfonates have a structural discontinuity at Sm/Eu whereas the R = $O_3SC_{10}H_7$-2 structure persists to Ln = Pr,[25] and the tosylate series changes to $[Ln(H_2O)_9](O_3SR)_3 \cdot 4H_2O$ for Ln = La, Ce, Nd.[13] In the case of the structurally uncharacterized **3–6**, the analytical compositions rule out $[Ln(H_2O)_9]_2(L)_3$ structures analogous to the tosylates[13] for the bulk solids. Even if, as is likely, the precursor crystals are more hydrated, it is probable that the structures contain coordinated 1,2-benzenedisulfonate ligands rather than solely coordinated water, since the structures of **14** and **15** (below) show that L^{2-} coordinates to La^{3+}, the largest lanthanoid, in both cationic and anionic species isolated from aqueous solution.

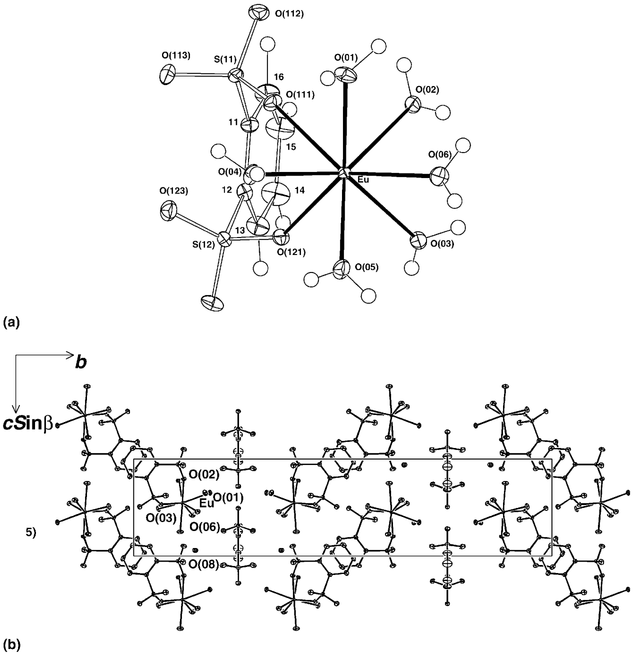

Fig. 2 (a) A representative $[LnL(H_2O)_6]^+$ cation (Ln = Eu (**8**)) from $[LnL(H_2O)_6]_2$ L · $4H_2O$, projected down the quasi-$\bar{4}$ axis of the (approximately) square-antiprismatic coordination environment. (b) The unit cell contents, projected down *a*; note the disposition of the anions in the mirror planes at y = 0.25, 0.75.

The packing in the unit cell is of interest, the (inversion related) aromatic rings of the coordinated L stacking up *a*,

Table 2 The metal atom environments in **$[LnL(H_2O)_6]_2[L]\cdot 4H_2O$**, (**8**, **13**, **2**). Presentation as in Table 1; values are given for Ln = Eu, above those for Ln = Lu and Ln = Y[a]

Atom	*r*	O(121)	O(01)	O(02)	O(03)	O(04)	O(05)	O(06)
O(111)	2.425(2)	72.77(6)	75.69(6)	75.48(7)	120.50(6)	77.09(7)	139.76(8)	143.82(8)
	2.356(2)	73.74(7)	75.05(7)	75.16(8)	120.99(7)	76.77(7)	140.10(8)	143.26(8)
	2.384(1)	73.38(2)	75.49(5)	75.30(5)	120.58(5)	77.06(5)	140.08(6)	143.46(6)
O(1121)	2.363(2)	—	143.88(6)	111.73(7)	74.37(7)	82.43(7)	80.06(7)	141.65(6)
	2.276(2)	—	144.15(7)	111.59(7)	73.85(7)	81.89(8)	79.25(7)	141.37(7)
	2.309(1)	—	144.13(5)	111.80(5)	74.03(5)	82.10(5)	79.51(5)	141.43(5)
O(01)	2.436(2)	—	—	76.15(8)	138.66(8)	73.71(8)	115.31(7)	73.61(7)
	2.341(2)	—	—	76.41(8)	139.06(9)	74.17(8)	115.99(7)	73.54(7)
	2.380(1)	—	—	76.37(6)	138.90(6)	73.94(6)	115.62(5)	73.50(5)
O(02)	2.392(2)	—	—	—	72.70(8)	143.25(7)	143.53(7)	78.98(7)
	2.297(2)	—	—	—	72.97(8)	143.51(7)	143.33(7)	79.35(8)
	2.336(2)	—	—	—	72.76(6)	143.48(5)	143.26(5)	79.01(5)
O(03)	2.431(2)	—	—	—	—	143.50(8)	78.14(8)	74.31(7)
	2.339(2)	—	—	—	—	142.78(8)	77.23(8)	74.63(7)
	2.380(1)	—	—	—	—	143.11(6)	77.62(6)	74.51(5)
O(04)	2.365(2)	—	—	—	—	—	70.28(7)	111.47(7)
	2.260(2)	—	—	—	—	—	70.73(7)	111.82(8)
	2.303(2)	—	—	—	—	—	70.58(5)	111.71(5)
O(05)	2.402(2)	—	—	—	—	—	—	72.32(8)
	2.307(2)	—	—	—	—	—	—	72.47(8)
	2.345(2)	—	—	—	—	—	—	72.43(6)
O(06)	2.406(2)	—	—	—	—	—	—	—
	2.310(2)	—	—	—	—	—	—	—
	2.354(1)	—	—	—	—	—	—	—

[a] Ln–O(111,1121)–S(11,12) are (Ln = Eu; Lu; Y) 159.8(1), 145.4(1); 159.4(1), 146.9(1), 159.67(9), 146.47(8)°, the Ln lying 2.972(5); 2.916(6); 2.937(4) Å out of the associated C_6 aromatic plane. The C_6(Ar)/(O(02,03; 111,121) interplanar dihedral angles are 76.08(9); 75.37(9); 75.43(7)°.

while those of the anions lie in the crystallographic mirror planes at *y* = 0.25, 0.75. All water molecule hydrogen atoms are involved in strong hydrogen-bonds, the hydrogen atoms of the two independent uncoordinated water molecules linking the anion and cation sulfonate oxygen atoms, while those of the coordinated water molecules link diversely to sulfonate and uncoordinated water molecule oxygen atoms. There are no hydrogen-bonds to coordinated water molecule oxygen atoms from any source (Table 4). Again, the linking of the complex cations to the anions through H-bonding provides a basis for ion pairing in methanol observed for **11**.

$[H_7O_3][La(C_6H_4(SO_2\cdot O)_2)_2]_{(\infty|\infty)}$, (14). The results of the single crystal X-ray structure determination of **14** are consistent with its formulation as a complex acid with an $[H_7O_3]^+$ cation and a LaL_2^- anion, the latter a single-stranded polymeric complex (Fig. 3(a)). The bond angles and distances about the lanthanum atom are shown in Table 5. Each

Table 3 Comparative coordinated and uncoordinated L geometries in **$[YL(H_2O)_6]_2[L]\cdot 4H_2O$** (**2**)

L	Coordinated	Uncoordinated
Distances (Å)		
S(n1,n2)–O(n11,n21)	1.460(1), 1.472(1)	1.452(2), 1.450(2)
S(n1,n2(O(n12,n22)	1.458(2), 1.449(2)	1.467(2), 1.469(2)
S(n1,n2)–O(n13,n23)	1.457(2), 1.457(2)	—
S(n1,n2)–C(n1,n2)	1.783(2), 1.789(2)	1.785(4), 1.777(3)
C(n1)–C(n2)	1.415(3)	1.421(4)
C(n1,n2)–C(n6,n3)	1.393(3), 1.388(3)	1.401(4), 1.390(5)
C(n6,n3)–C(n5,n4)	1.390(3), 1.394(3)	1.387(7), 1.391(5)
C(n4)–C(n5)	1.383(4)	1.376(6)
Angles (degrees)		
C(n1,n2)–S(n1,n2)–O(n11,n21)	106.26(8), 105.08(9)	107.69(9), 106.89(8)
C(n1,n2)–C(n1,n2)–O(n12,n22)	105.6(1), 106.80(9)	105.1(1), 106.0(1)
C(n1,n2)–S(n1,n2)–O(n13,n23)	108.4(1), 108.03(9)	—
O(n11,n21)–S(n1,n2)–O(n12,n22)	112.23(9), 111.17(8)	110.82(8), 111.97(7)
O(n11,n12)–S(n1,n2)–O(n13,n23)	112.74(9), 112.48(8)	114.2(1), 112.6(1)
O(n12,n22)–S(n1,n2)–O(n13,n23)	111.12(9), 112.8(1)	—
S(n1,n2)–C(n1,n2)–C(n2,n1)	124.5(1), 124.7(1)	125.6(2), 124.6(3)
S(n1,n2)–C(n1,n2)–C(n6,n3)	116.1(2), 116.1(2)	116.1(2), 115.8(2)
C(n2,n1)–C(n1,n2)–C(n6,n3)	119.4(2), 119.2(2)	118.3(3), 119.6(3)
C(n1,n2)–C(n6,n3)–C(n5,n4)	120.7(2), 120.8(2)	121.1(3), 120.6(3)
C(n6,n3)–C(n5,n4)–C(n4,n5)	120.0(2), 120.0(2)	120.1(3), 120.3(4)

Table 4 Hydrogen-bonding in **$[LnL(H_2O)_6]_2[L]\cdot 4H_2O$**. Values given are the H···O distance (refined) from the Ln = Eu determination, followed by the associated O···O distance for the Ln = Eu, Lu, Y complexes (**8**, **13**, **2**)

Atoms		Distance/Å
O(01),	H(01a)···O(211)	1.95(7); 2.792(4), 2.805(4), 2.802(3)
	H(01b)···O(222[a])	2.02(5); 2.808)3), 2.831(3), 2.821(2)
O(02),	H(02a)···O(08[b])	1.82(5); 2.668(3), 2.660(3), 2.668(2)
	H(02b)···O(123[c])	2.26(5); 2.884(4), 2.904(3), 2.889(2)
O(03),	H(03a)···O(123[c])	2.02(6); 2.864(3), 2.860(4), 2.861(3)
	H(03b)···O(122[d])	2.04(6); 2.740(3), 2.753(3), 2.743(2)
O(04),	H(04a)···O(07)	1.80(4); 2.655(3), 2.652(3), 2.655(2)
	H(04b)···O(221[a])	1.86(5); 2.671(3), 2.672(3), 2.677(2)
O(05),	H(05a)···O(113[e])	1.91(4); 2.834(3), 2.871(3), 2.865(2)
	H(05b)···O(08)	1.91(6); 2.681(3), 2.685(3), 2.691(3)
O(06),	H(06a)···O(112)	2.23(4); 2.881(3), 2.881(3), 2.881(2)
	H(06b)···O(07[e])	1.92(5); 2.747(4), 2.729(4), 2.735(3)
O(07),	H(07a)···O(113)	1.89(5); 2.947(3), 2.899(3), 2.925(2)
	H(07b)···O(212[f])	1.94(5); 2.814(2), 2.801(2), 2.803(2)
O(08),	H(08a)···O(112[a])	1.99(5); 2.735(3), 2.720(3), 2.731(2)
	H(08b)···O(211[a])	2.03(5); 2.781(3), 2.778(3), 2.782(2)

[a] Transformation of the asymmetric unit: x, y, $1 + z$. [b] Transformation of the asymmetric unit: x , y, $z - 1$. [c] Transformation of the asymmetric unit: $x + 1$, y, z. [d] Transformation of the asymmetric unit: $1 - x$, $\bar{y}$, $1 - z$. [e] Transformation of the asymmetric unit: $x + 1$, y, $1 + z$. [f] Transformation of the asymmetric unit: $x - 1$, y, z.

lanthanum centre is octacoordinated by a single oxygen atom from each of eight sulfonate groups of four ligands in a distorted square antiprismatic array. This polymeric structure contrasts with all others in this paper, and resembles the LnL_2^- (Ln = La, Nd) chains of $[K(H_2O)_2LnL_2]_n$.[18]

Each ligand binds in a μ-η^2(O,O′):η^2(O″,O‴) fashion with two oxygen atoms from each sulfonate group (O,O″ from one; O′,O‴ from the other) bridging pairs of adjacent lanthanum ions. The same oxygen atoms also chelate the metal centres with O,O′ from different sulfonate groups bound to one La, and O″, O‴ to the other giving seven-membered chelate rings similar to the binding in **2**, **7–13**. Thus, each sulfonate group has an oxygen atom that is not ligated, and these are involved in hydrogen-bonding to the oxonium ion. The La(1)–O distances range from 2.440–2.547(3) Å (⟨La–O⟩ 2.49(3) Å), similar to other $La–O_{sulfonate}$ values.[29] Closer examination shows that ligand S(11,12) binds differently from ligand S(21,22). In the former, one bridging sulfonate group La(1)–O(113)–S(11)–O(112)–La(1′) is oriented so that O(112) is located 3.091(2) Å from La(1). All other ligated oxygen

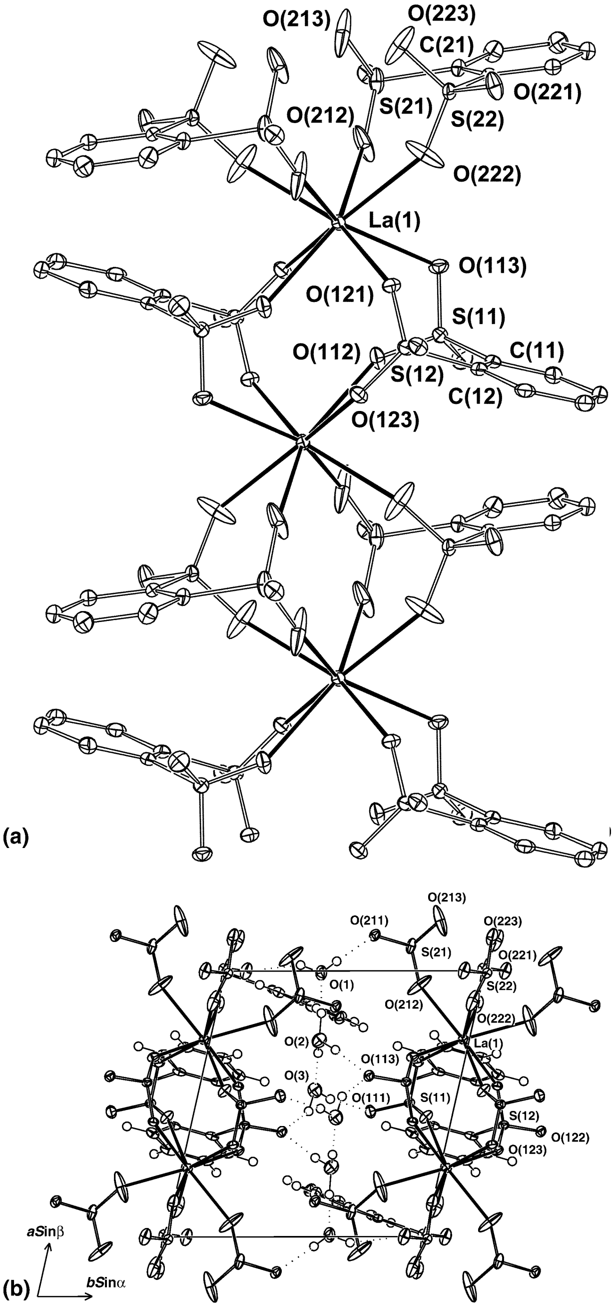

Fig. 3 (a) The polymeric chain in $[H_7O_3][LaL_2]_{(\infty|\infty)}$. (b) Unit cell contents projected down c, showing the hydrogen-bonding.

Table 5 The lanthanum environment in $[H_7O_3]$ $[LaL_2]$ (**14**). Presentation as in Table 1; θ is the associated La–O–S angle

Atom	r	O(121)	O(212)	O(222)	O(112[a])	O(123[a])	O(213[b])	O(223[b])	θ/°
O(113)	2.547(2)	77.62(7)	77.64(8)	73.21(9)	112.42(7)	86.37(8)	140.62(11)	147.98(9)	113.6(1)
O(121)	2.486(3)	—	139.89(9)	76.35(9)	73.07(8)	123.61(8)	76.76(10)	139.27(8)	147.4(2)
O(212)	2.488(3)	—	—	69.63(11)	144.84(11)	79.75(10)	113.56(11)	74.98(9)	153.3(2)
O(222)	2.468(4)	—	—	—	145.00(9)	146.00(7)	76.01(10)	111.52(11)	147.3(2)
O(112[a])	2.494(2)	—	—	—	—	67.90(8)	80.75(10)	82.36(8)	152.8(1)
O(123[a])	2.525(3)	—	—	—	—	—	131.84(9)	72.76(10)	141.0(1)
O(213[b])	2.485(4)	—	—	—	—	—	—	67.45(11)	152.4(2)
O(223[b])	2.440(3)	—	—	—	—	—	—	—	163.4(2)

[a] Transformation of the asymmetric unit: $1 - x$, $2 - y$, $\bar{z}$. [b] Transformation of the asymmetric unit: $2 - x$, $2 - y$, $\bar{z}$.

atoms are > 3.5 Å from a second lanthanum atom. Thus, it is possible to regard La(1)–O(112) as a weak interaction, and the sulfonate group as μ-η^2:η^1 bonded (analogous to tridentate carboxylates), and the ligand binding as μ-η^2(O,O′):η^1(O):η^2(O″,O‴). In $[K(H_2O)NdL_2]_n$, there is also such a tridentate sulfonate group with highly unsymmetrical chelation (0.5 Å) to one Nd atom and a long Nd–O bond (2.943(4) Å), which, from ionic radii,[21] would extrapolate to La–O *ca.* 3.00 Å, rather shorter than observed for **14**. Examination of the Cambridge Crystallographic Database for La–O bond lengths in carboxylate complexes reveals credible values up to 3.1 Å. The average of the eight short La–O distances for this ligand (2.51 Å) is somewhat longer than for ligand S(21,22) (2.47 Å) and this elongation could be considered to reflect involvement in an additional interaction. Thus, lanthanum might be viewed as nine-coordinate (or better, *ca.* 8.5).

Hydrophobic layers of the aromatic groups of the ligands intercalate between the columns of the hydrophilic metal complex, the closest contact distance between two points in adjacent benzene rings being *ca.* 3.45 Å for C(25)···C(26′). All hydrogen atoms in the structure are credibly located and refinable in $(x,y,z,U_{\mathrm{iso}})_{\mathrm{H}}$, and suggest the triad of water molecules (O(1,2,3) to be a rare example[30] of an $H_7O_3^+$ oxonium ion that balances the charge of the $[LaL_2]^-$ complex anion (Fig. 3(b)). The O(1)···O(2)···O(3) angle is 123.4(3)°, which is marginally more obtuse than those of other similar arrays which lie in the range 105–116°, with the O(2)···O(1,3) distances 2.451(4), 2.541(4) Å also similar to literature values.[30] The asymmetry in the O···O bond distances is typical for these types of ions because the ion can be regarded as a hydrated $H_5O_2^+$ ion, which, when isolated, has a very short O···O distance (less than 2.48 Å).[30] All O···O bond distances in the $H_7O_3^+$ ion (Table 6) are shorter than typical hydrogen-bonded systems due to delocalisation of the positive charge at the central O atom. The hydrogen atoms on the terminal oxygen atoms of the $H_7O_3^+$ ion, O(1,3), hydrogen-bond to uncoordinated sulfonate oxygen atoms (Table 6) at distances H···O > 1.91(7), (O···O > 2.724(5) Å). One hydrogen atom bound to the central oxygen atom (O(2)) hydrogen bonds to a sulfonate oxygen atom at a short H···O distance (H(b)···O(122) 1.76(4) Å; also shorter O···O 2.659(3) Å). This distance is comparable to the hydrogen bonding distances within the $H_7O_3^+$ ion (H(a)···O 1.45(6), O(2)···O(1) 2.451(4) Å and H(c)···O 1.78(4), O(2)–O(3) 2.541(4) Å) and reflects the influence of the charge associated with the central H_3O^+ ion. The H_3O^+ array at O(2) is pyramidal (ΣH–O–H *ca.* 342°).

Table 6 Hydrogen-bonding in $[H_7O_3][LaL_2]$ (**14**)

Atoms		Distance/Å
O(1),	H(1a)···O(211)	2.724(5), 1.91(7)
	H(1b)···O(221^a)	2.816(4), 2.06(5)
O(2),	H(2a)···O(1)	2.451(4), 1.45(6)
	H(2b)···O(122^b)	2.659(3), 1.76(4)
	H(2c)···O(3)	2.541(4), 1.78(4)
O(3),	H(3a)···O(111)	2.815(5), 2.04(6)
	H(3b)···O(122^a)	2.815(5), 2.03(6)

^{a} Transformation of the asymmetric unit: x, $y - 1$, z. ^{b} Transformation of the asymmetric unit: $1 - x$, $2 - y$, $\bar{z}$.

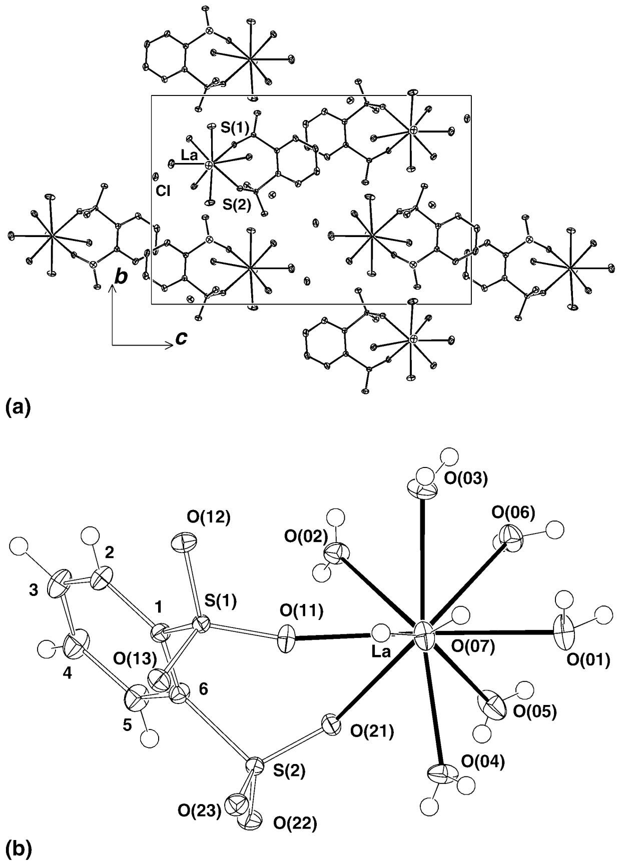

Fig. 4 (a) Unit cell contents of $[LaL(H_2O)_7]Cl\cdot H_2O$ (**15**) projected down *a*. (b) Projection of the cation showing the quasi-capped square antiprismatic aspect of the La coordination environment.

With a polymeric structure and one oxygen per sulfonate group available for coordination on scission of H-bonds, **14** is an excellent potential precursor for bimetallic networks. The acid functionality provides a basis for reactions with hydroxides, oxides, carbonates, acetates *etc.*, and the preparation of **14** is simple and high yielding (eqn (4) and (5)).

$[La(C_6H_4(SO_2\cdot O)_2)(H_2O)_7]Cl\cdot H_2O$, (15). The results of the single crystal X-ray study are consistent with the above ionic formulation and connectivity, one formula unit, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. The cation is similar to those previously described in **2**, **7**, **8**, **10**, **12**, **13**, but, with the largest of the lanthanoid atoms now at its centre, an additional water molecule is coordinated, the stereochemistry of the resulting nine-coordinate ion becoming a capped square antiprism (Fig. 4, Table 7). Hydrogen-bonding from the water molecule hydrogen atoms (Table 8) is extensive and mainly directed along *a*, to the sulfonate oxygen atoms of adjacent molecules, the tendency to columnar formation assisted by interactions with the chloride ions. The aromatic rings also interleave somewhat in the same dimension. The lengthening of ⟨La–$O_{\mathrm{sulfonate}}$⟩ and ⟨La–OH_2⟩ from the corresponding values for $[SmL_2(H_2O)_6]^+$ is in close accordance with the increase in ionic radius and the change of coordination number.[21] On the other hand, the lengthening of ⟨Ln–$O_{\mathrm{sulfonate}}$⟩ over that for

Table 7 The lanthanum environment in $[LaL(H_2O)_7]Cl \cdot H_2O$ (**15**). Presentation as in Table 1

Atom	r/Å	O(21)	O(01)	O(02)	O(03)	O(04)	O(05)	O(06)	O(07)
O(11)	2.514(2)	67.53(7)	133.57(8)	75.46(7)	84.81(8)	87.60(8)	134.92(9)	140.18(8)	66.50(7)
O(21)	2.505(2)	—	139.26(9)	70.74(8)	137.53(9)	69.99(8)	67.54(9)	116.99(8)	119.21(8)
O(01)	2.571(3)	—	—	139.92(8)	83.12(10)	76.16(9)	81.99(11)	71.28(8)	67.09(9)
O(02)	2.516(2)	—	—	—	71.50(9)	140.66(8)	93.22(9)	70.18(8)	129.52(8)
O(03)	2.555(2)	—	—	—	—	142.89(9)	133.38(8)	65.84(8)	73.15(8)
O(04)	2.523(3)	—	—	—	—	—	73.92(9)	132.03(8)	70.53(8)
O(05)	2.543(3)	—	—	—	—	—	—	67.54(8)	137.18(9)
O(06)	2.616(2)	—	—	—	—	—	—	—	123.80(8)
O(07)	2.547(3)	—	—	—	—	—	—	—	—

$[H_7O_3{}^+][LaL_2]$ is less than expected for the change in coordination number and may reflect the influence of charge of the complex. Isolation of **15**, which contains a $[LnL(H_2O)_7]^+$ complex cation from water, makes it unlikely that **3**, and hence **4–6**, simply contain $[Ln(H_2O)_n]^{3+}$ ions and L^{2-} counterions.

Conclusions

The dominant theme from the interactions of rare earth ions with 1,2-benzenedisulfonate (L^{2-}) ions in water is formation of mononuclear $[LnL(H_2O)_n]^+$ complex cations (Ln = La, n = 7; Ln = Y, Sm–Lu, n = 6) with variously Cl^-, $[SmL_2(H_2O)_4]^-$ and L^{2-} counterions. In these, as well as in $[SmL_2(H_2O)_4]^-$, L chelates through one oxygen per sulfonate group resulting in seven-membered chelate rings. Eight-coordination is omnipresent except in $[LaL(H_2O)_7]Cl$ (**15**), but Ln = Ce–Nd (**3–6**) remain structurally uncertain through lack of suitable crystals. By contrast with the mononuclear complexes, $[H_7O_3][LaL_2]$ (**14**), has a polymeric structure with μ-η^2:η^2-disulfonate ligands bridging adjacent La atoms and also forming seven-membered chelate rings with each La atom. An additional possible longer interaction gives La a hint of nine-coordination. Apart from involvement in H-bonding, aqua ligands are solely unidentate, by contrast with the observation of bridging H_2O ligands in $[La(MeSO_3)_3(H_2O)_2]$.[31] In all structures there are uncoordinated sulfonate oxygen atoms making all complexes, and particularly **14**, potential reagents for building bimetallic polymers and networks, as supported by structural similarities between **14** and the network $[K(H_2O)LnL_2]_n$.[18]

Experimental

General

The rare earth oxides used were from Grace Davison Chemicals, Unilab, Riedel de Haën and Allied Signal, cerium(III) carbonate and dipotassium 1,2-benzenedisulfonate from Aldrich, and the perfluoroadipic acid from Bristol Organic Limited. 1,2-Benzenedisulfonic acid was prepared by ionic exchange as outlined in the literature,[18] but, instead of dipotassium 1,2-benzenedisulfonic acid monohydrate, the anhydrous compound was used. No potassium could be detected in solutions of the acid.[32] The metal analysis procedures were adapted from the method described previously,[33] but without the need of an acid digestion for all metals except scandium, which required the full digestion to obtain a sharp end-point. The Campbell Microanalytical Laboratory of the University of Otago, New Zealand, performed the microanalyses. Listed infrared data, acquired using a Perkin Elmer 1600 FTIR spectrometer, are of Nujol and hexachlorobutadiene mulls for the region 4000–650 cm^{-1}. ^{1}H-NMR spectra were recorded at 400 MHz with a Bruker DRX400 spectrometer. Electrospray mass spectra were recorded with a Bruker BioApec 47e FTMS with a 4.7 T superconducting magnet and fitted with an Analytica Electrospray Source. Only metal containing peaks are quoted, L in the mass spectral assignments referring to the benzene-1,2-disulfonate ligand. Visible/near IR spectra were recorded with a Varian-Cary 17 spectrophotometer. Molar absorption coefficients (ε) are given in mol dm^{-3} cm^{-1}. All compounds were unmelted to 360 °C.

Table 8 Hydrogen-bonding in **$[LaL(H_2O)_7]Cl \cdot H_2O$ (15)**

Atoms		Distance/Å
O(01),	H(01a)···Cl^a	3.099(3), 2.2
	H(01b)···Cl^b	3.231(3), 2.3
O(02),	H(02a)···O(08)	2.754(4), 1.8
	H(02b)···O(13^a)	2.741(3), 2.1
O(03),	H(03a)···O(08^c)	2.748(4), 1.9
	H(03b)···O(22^c)	2.946(4), 2.2
O(04),	H(04a)···Cl	3.120(3), 2.3
	H(04b)···O(12^d)	2.796(4), 2.2
O(05),	H(05a)···O(12^e)	2.779(4), 2.0
	H(05b)···O(21)	2.806(4), 2.6
O(06),	H(06a)···Cl^a	3.430(3), 2.8
	H(06b)···O(23^a)	2.876(3), 2.0
O(07),	H(07a)···O(22^f)	2.755(4), 1.9
	H(07b)···Cl^g	3.140(3), 2.2
O(08),	H(08a)···O(23^a)	2.782(4), 2.3
	H(08b)···Cl^h	3.165(3), 2.3

[a] Transformation of the asymmetric unit: $x - 1, y, z$. [b] Transformation of the asymmetric unit: $x, {}^3/_2 - y, \bar{z}$. [c] Transformation of the asymmetric unit: $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$. [d] Transformation of the asymmetric unit: $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$. [e] Transformation of the asymmetric unit: $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$. [f] Transformation of the asymmetric unit: $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$. [g] Transformation of the asymmetric unit: $x - \frac{1}{2}, {}^3/_2 - y, \bar{z}$. [h] Transformation of the asymmetric unit: ${}^3/_2 - x, 1 - y, \frac{1}{2} + z$.

General syntheses of $[Ln_2L_3]$

1,2-Benzenedisulfonic acid and the appropriate lanthanide(III) oxide were refluxed in water. The mixture was then filtered though a Celite pad and the water evaporated to dryness. The crude product was then redissolved in the minimum amount of water and refiltered though Celite and the solvent was removed until the solution became viscous when it was left to crystallize. In some cases (**3–6**) ethanol was added to aid crystallization. The product was then collected and drained on a sinter.

Synthesis of [Sc_2L_3]·14H_2O (1). 1,2-Benzenedisulfonic acid (2.48 mmol) and scandium(III) oxide (0.56 g, 4.06 mmol) were refluxed in water (60 mL) for 21 h. Work-up of the solution yielded complex (**1**) as a white powder. Yield: 0.75 g (86%). $C_{18}H_{40}O_{32}S_6Sc_2$ (1050.79); C 20.51, 20.46 (calc. 20.57); H 3.58, 3.56 (3.84); Sc 9.61 (8.56)%. IR: [cm^{-1}]: ν = 3354m, 2958w, 2928w, 2853w, 1637m, 1570m (sh), 1457w, 1434m, 1292m (sh), 1243s, 1189s, 1162vs, 1132vs, 1062s, 1037m, 1004w, 758m, 722m, 695s. ^{1}H-NMR (D_2O): δ = 7.66 (m, 6H, **H**4,5); 8.12 (m, 6H, **H**3,6). *m/z* (−ve ES, 40v) 517 (100%, [ScL_2]$^-$), 549 (21.0, [ScL_2(MeOH)]$^-$), 793 (3.2), 843 (14.0, [Sc_2L_3(EtO)]$^-$), 1035 (3.8, [Sc_2L_3(HL)]$^-$)

Synthesis of [YL(H_2O)$_6$]$_2$[L]·4H_2O (2). Yttrium(III) oxide (0.80 g, 3.54 mmol) and 1,2-benzenedisulfonic acid (2.48 mmol) were refluxed in water (~40 mL) for 28 h. The reaction mixture was worked up as above, giving colourless single crystals of (**2**). Yield: 0.10 g (11%). $C_{18}H_{44}O_{34}S_6Y_2$ (1173.15); C 18.84, 19.00 (calc. 18.40); H 3.44, 3.49 (3.78); Y 15.12 (15.15)%. IR: [cm^{-1}]: ν = 3473s, 3365s, 3201s (overall br feature), 2958w, 2923w, 2853w, 1657m, 1456w, 1492w, 1236m (sh), 1201vs, 1175s, 1131vs, 1079m, 1060s, 1039m, 1005m, 890w, 843w, 759m, 724w, 696m. ^{1}H-NMR (D_2O): δ = 7.69 (m, 6H, **H**4,5); 8.14 (m, 6H, **H**3,6). *m/z* (−ve ES, 35v) 561 (100%, [YL_2]$^-$), 593 (17.8, [YL_2(MeOH)]$^-$), 647 (29.6, [YL_2(MeOH)(H_2O)$_3$]$^-$), 843 (2.5, [Y_2L_2(MeO)$_2$(H_2O)(O_2CCF_3)]$^-$).

Synthesis of [La_2L_3]·7H_2O (3). 1,2-Benzenedisulfonic acid (2.61 mmol) was added to lanthanum(III) oxide (1.04 g, 3.19 mmol) and the reaction mixture stirred in water (*ca.* 70 mL), and brought to reflux for 6 h at 120 °C. After work-up of the mixture, attempts to produce single crystals from water and water/ethanol solutions afforded feathery, colourless crystalline material unsuitable for the X-ray work. Yield: 1.09 g (100%). $C_{18}H_{26}La_2O_{25}S_6$ (1112.59); C 19.57 (calc. 19.43); H 2.43 (2.50); La 24.79 (24.97)%. IR: [cm^{-1}]: ν = 3417m (vbr), 2961w, 2928w, 2850w, 1633m, 1458m, 1431m, 1376w, 1292sh, 1268sh, 1246vs, 1207sh, 1157s, 1132vs, 1065vs, 1052sh, 1036s, 1013m, 874m, 856m, 766m, 760m, 721w, 693s, 668m. ^{1}H-NMR (D_2O): δ = 1.19 (t, 1H, **C**H_3CH_2OH); 3.65 (q, 0.8H, CH_3**C**H_2OH); 7.69 (m, 6H, **H**4,5); 8.14 (m, 6H, **H**3,6). *m/z* (+ve ES, 50v) 375 (70.3%, [LaL]$^+$), 453 (100, [LaL(Me_2SO)]$^+$), 531 (44.3, [LaL(Me_2SO)$_2$]$^+$); (−ve ES, 50v) 611 (100%, [LaL_2]$^-$), 893 (8.3, [LaL_2(H_2O)$_3$(MeOH)$_4$]$^-$).

Synthesis of [Ce_2L_3]·6H_2O (4). $Ce_2(CO_3)_3\cdot 11H_2O$ (3.68 g, 5.59 mmol) was added to 1,2-benzenedisulfonic acid (2.74 mmol) in water (*ca.* 70 mL). The mixture was brought to reflux for 10 h at 120 °C, and, after work-up, ethanol was added resulting in the deposition of a white powder immediately after addition, which was found to be (**4**). Yield: 0.81 g (81%). $C_{18}H_{24}Ce_2O_{24}S_6$ (1095.71); Ce 25.52 (25.55)%. IR: [cm^{-1}]: ν = 3495s (vbr), 2950w, 2922w, 2850w, 1622s, 1455w, 1433s, 1240vs, 1161s, 1132vs (br), 1065vs, 1037vs, 1012s, 878w, 768s, 695vs, 665s. ^{1}H-NMR (D_2O): δ = 7.49 (m, 6H, **H**4,5); 7.87 (m, 6H, **H**3,6). *m/z* (+ve ES, 50v) 376 (32.5%, [CeL]$^+$), 454 (100, [CeL(Me_2SO)]$^+$), 532 (71.3, [CeL(Me_2SO)$_2$]$^+$); (−ve ES, 50v) 612 (100%, [CeL_2]$^-$), 894 (1.9, [CeL_2(H_2O)$_3$(MeOH)$_4$]$^-$).

Synthesis of [Pr_2L_3]·12H_2O (5). A similar preparation from praseodymium(III/IV)) oxide (2.20 g, 2.15 mmol) and 1,2-benzenedisulfonic acid (2.48 mmol) in water (50 mL) was employed, but with a reaction time of 20 h under reflux, a green crystalline product of (**5**) being obtained. Yield 0.32 g (33%). $C_{18}H_{32}O_{28}Pr_2S_6$ (1170.63); C 18.39, 18.36 (calc. 18.47); H 1.95, 2.24 (2.78)%. IR: [cm^{-1}]: ν = 3375m (vbr), 2961w, 2927w, 2853w, 1622m, 1458w, 1435m, 1249s, 1161vs, 1132vs, 1065vs, 1056s (sh), 1040m, 1012m, 760m, 693s. ^{1}H-NMR (D_2O): δ = 7.09 (m, 6H, **H**4,5); 7.40 (m, 6H, **H**3,6). *m/z* (−ve ES, 50v) 613 (100%, [PrL_2]$^-$), 1035 (5.7, [Pr_2L_3(HCO_2)]$^-$). Visible/near IR [λ_{max}, nm (ε), H_2O]: 444 (3), 469 (9), 482 (8), 889 (4).

Synthesis of [Nd_2L_3]·9H_2O·EtOH (6). Neodymium(III) oxide trihydrate (2.14 g, 5.48 mmol) was refluxed at 110 °C with 1,2-benzenedisulfonic acid (2.74 mmol) in water (*ca.* 100 mL) for 12 h. A light pink, feathery crystalline material formed and was found to be (**6**). Yield: 0.72 (65%). $C_{20}H_{36}Nd_2O_{28}S_6$ (1205.35); C 19.94 (calc. 19.93); H 2.60 (3.01); Nd 23.92 (23.93)%. IR: [cm^{-1}]: ν = 3385m (vbr), 2964m, 2921m, 2851m, 1634m, 1455m, 1433m, 1248s, 1224s, 1201s (sh), 1179vs, 1132vs, 1060s, 1038m, 1010m, 886w, 764m, 696s. ^{1}H-NMR (D_2O): δ = 1.01 (t, 3H, **C**H_3CH_2OH); 3.48 (q, 2H, CH_3**C**H_2OH); 7.50 (m, 6H, **H**4,5); 7.88 (m, 6H, **H**3,6). *m/z* (−ve ES, 50v) 616 (100%, [NdL_2]$^-$), 684 (7.8, [NdL_2(H_2O)$_2$(MeOH)]$^-$). Visible/near IR [λ_{max}, nm (ε), H_2O]: 329 (5), 338 (3), 347 (7), 354 (9), 418 (2), 427 (2), 461 (2), 469 (2), 475 (2), 512 (4), 522 (9), 576 (16), 623 (1), 679 (1), 732 (9), 740 (14), 794 (21), 799 (14), 865 (7), 889 (1).

Synthesis of [SmL(H_2O)$_6$][SmL_2(H_2O)$_4$]·'$8\frac{1}{4}H_2O$' (7), bulk analytical composition [Sm_2L_3]·13H_2O. Samarium(III) oxide (1.21 g, 3.20 mmol) and 1,2-benzenedisulfonic acid (2.47 mmol) were refluxed in water (50 mL) for 23 h. Pale yellow crystals of **7** deposited in the flask after work up. Yield: 0.69 g (67%)·$C_{18}H_{38}O_{31}S_6Sm_2$ (1243.58); C 17.83, 17.84 (calc. 17.85); H 2.73, 2.50 (2.83); Sm 24.44 (24.19)%. IR: [cm^{-1}]: ν = 3500m (vbr), 2961w, 2922w, 2856w, 1618m, 1460w, 1432m, 1268s, (sh), 1257s, 1162vs, 1135vs, 1067vs, 1040m, 1014m, 972w, 769m, 721m, 696s, 670m. ^{1}H-NMR (D_2O): δ = 7.65 (m, 6H, **H**4,5); 8.10 (m, 6H, **H**3,6). *m/z* (−ve ES, 50v) 626 (100%, [SmL_2]$^-$). Visible/near IR [λ_{max}, nm (ε), H_2O]: 344 (5), 362 (5), 374 (4), 390 (3), 401 (8), 416 (3), 440 (2), 464 (2), 479 (2), 950 (1), 1087 (5), 1243 (6). Mol. cond. (S cm^2 mol^{-1}) in H_2O: 415 (1.58×10^{-3} M); in MeOH: 43 (1.65×10^{-3} M).

Synthesis of [EuL(H_2O)$_6$]$_2$[L]·4H_2O (8), bulk analytical composition [Eu_2L_3]·14H_2O. Europium(III) oxide (1.15 g, 3.27 mmol) was added to 1,2-benzenedisulfonic acid

(2.47 mmol) and the reaction mixture stirred in water (*ca.* 80 mL). The mixture was brought to reflux for 19 h. Colourless crystals of (**8**) deposited from the aqueous solution, which exhibited a red fluorescence upon irradiation with UV light. Yield: 0.12 g (12%). $C_{18}H_{40}Eu_2O_{32}S_6$ (1264.80); C 17.00; 16.88 (calc. 17.05); H 3.25; 3.19 (3.42); Eu 23.52 (23.31)%. IR: [cm^{-1}]: ν = 3433m, 2961w, 2922w, 2856w, 1613m, 1457w, 1429w, 1400w, 1301m (sh), 1246s, 1163vs, 1132vs, 1063vs, 1039m (sh), 1014m (sh), 760m 720m, 693vs, 671s. ^{1}H-NMR (D_2O): δ = 7.59 (m, 6H, **H**4,5); 8.11 (m, 6H, **H**3,6). *m*/*z* (−ve ES, 25v) 625 (100%, [EuL_2]$^-$), 863 (4.2, [EuL$(LH)_2$]$^-$).

Synthesis of [GdL$(H_2O)_6$]$_2$[L]·4H_2O (9), bulk analytical composition [Gd_2L_3]·15H_2O. Gadolinium(III) oxide (1.16 g, 3.20 mmol) was added to a round-bottomed flask containing water (50 mL) and 1,2-benzenedisulfonic acid (2.47 mmol). The mixture was refluxed for 24 h, work-up of the solution being as for (**1**), giving colourless crystals of (**9**). Yield: 0.47 g (44%). $C_{18}H_{42}Gd_2O_{33}S_6$ (1293.39); C 16.70 (calc. 16.72); H 3.29 (3.27); Gd 24.33 (24.32)%. IR: [cm^{-1}]: ν = 3480vs, 3367vs, 3200vs (overall br feature), 2956w, 2922w, 2860w, 1654m, 1454w, 1431w, 1241s (sh), 1202vs, 1175m (sh), 1162m (sh), 1140m (sh), 1130vs, 1079m, 1060s, 1038m, 1011m (sh), 1004m, 963w, 926w, 763m, 697s. *m*/*z* (−ve ES, 50v) 630 (24.1%, [GdL_2]$^-$). (+ve ES 50v) 204 (100%, [Gd(CH_2O_2)]$^+$), 248 (100, [Gd$(CH_2O_2)_2$]$^+$), 394 (82.3, [GdL]$^+$), 426 (33.5, [GdL(MeOH)]$^+$), 467 (42.4), 490 (22.2, [GdL$(MeOH)_3$]$^+$), 522 (18.4, [GdL$(MeOH)_4$]$^+$).

Synthesis of [TbL$(H_2O)_6$]$_2$[L]·4H_2O (10), bulk analytical composition [Tb_2L_3]·14H_2O. Terbium(III/IV) oxide (1.20 g) was refluxed with a solution of 1,2-benzenedisulfonic acid (2.47 mmol) in water (∼80 mL). The mixture was refluxed for 24 h, work-up of the solution producing colourless crystals of (**10**), which exhibited a green fluorescence when irradiated with UV light. Yield: 0.36 g (33%). $C_{18}H_{40}O_{32}S_6Tb_2$ (1278.73); C 16.87; 16.64 (calc. 16.87); H 3.07; 3.12 (3.38); Tb 24.85 (24.12)%. IR: [cm^{-1}]: ν = 3360m (vbr), 2955w, 2922w, 1621m, 1470w, 1462w, 1454w, 1429w, 1235s, 1163vs, 1133vs, 1064vs, 1040m (sh), 1011s, 761m, 721w, 695s. ^{1}H-NMR (D_2O): δ = 8.14 (m, 6H, **H**4,5); 9.06 (m, 6H, **H**3,6). *m*/*z* (−ve ES, 25v) 631 (41.7%, [TbL_2]$^-$), 869 (2.2, [TbL$(LH)_2$]$^-$).

Synthesis of [HoL$(H_2O)_6$]$_2$[L]·4H_2O (11), bulk analytical composition [Ho_2L_3]·13H_2O. 1,2-Benzenedisulfonic acid (2.64 mmol) was added to holmium(III) oxide (0.71 g, 1.88 mmol) and the reaction mixture stirred in water (*ca.* 80 mL). The mixture was brought to reflux overnight, with pale pink crystals of (**11**) depositing from the aqueous solution after work-up. Yield: 0.66 g (57%). $C_{18}H_{38}Ho_2O_{31}S_6$ (1271.83); C 16.54, 16.50 (calc. 16.98); H 3.44, 3.32 (3.01); Ho 26.11 (25.94)%. IR: [cm^{-1}]: ν = 3406s (vbr), 2955w, 2921w, 2860w, 1656m, 1626m, 1454w, 1429w, 1271s (sh), 1257vs, 1166vs, 1135vs, 1068vs, 1041m, 1012m, 10 004m, 971w, 963w, 890w, 766s, 720m, 696s. *m*/*z* (−ve ES, 35v) 491 (12.2%, [HoL$(HCO_2)_2$]$^-$), 559 (9), 637 (100, [HoL_2]$^-$), 669 (5.8, [HoL_2(MeOH)]$^-$), 705 (6.4, [HoL_2(MeOH)$(H_2O)_2$]$^-$), 773 (6.1, [$HoL_2(MeOH)_2(H_2O)_4$]$^-$), 919 (5.8). Visible/near IR [λ_{max}, nm (ε), H_2O]: 333 (11), 345 (10), 361 (12), 386 (8), 417 (10), 451 (14), 468 (6), 473 (6), 485 (8), 537 (13), 641 (9), 656 (5), 891 (2), 1153 (3), 1188 (3). Mol. cond. (S cm^2 mol^{-1}) in H_2O: 376 (1.16 × 10^{-3} M); in MeOH: 60 (1.05 × 10^{-3} M).

Synthesis of [YbL$(H_2O)_6$]$_2$[L]·4H_2O (12). Ytterbium(III) oxide (0.85 g, 2.15 mmol) and 1,2-benzenedisulfonic acid (2.64 mmol) were refluxed in water (∼80 mL) for 26.5 h. Work-up was as for complex (**1**), affording colourless crystals of (**12**). Yield: 0.27 g (23%). $C_{18}H_{44}O_{34}S_6Yb_2$ (1342.99); C 16.12, 16.15 (calc. 16.10); H 3.25, 3.32 (3.30); Yb 24.98 (25.77)%. IR: [cm^{-1}]: ν = 3464s, 3344s, 3189s (overall br feature), 2922w, 1642m, 1453w, 1428w, 1407w, 1240s (sh), 1211 and 1199vs, 1178s (sh), 1132vs, 1080s, 1061s, 1040s, 1013s, 1004s, 938w, 790s, 746w 698vs. ^{1}H-NMR (D_2O): δ = 8.09 (m, 6H, **H**4,5); 8.59 (m, 6H, **H**3,6). *m*/*z* (−ve ES, 35v) 646 (100%, [YbL_2]$^-$). Visible/near IR [λ_{max}, nm (ε), H_2O]: 950 (5), 974 (8).

Synthesis of [LuL$(H_2O)_6$]$_2$[L]·4H_2O (13). An excess of lutetium(III) oxide (0.34 g, 0.85 mmol) was added to a stirred aqueous solution (40 mL) of 1,2-benzenedisulfonic acid (0.99 mmol) and the reaction mixture refluxed for 17 h. After work-up of the solution discrete colourless crystals of (**13**) were obtained. Yield: 0.15 g (57%). $C_{18}H_{44}Lu_2O_{34}S_6$ (1346.58); C 16.17 (calc. 16.05); H 3.19 (3.29)%. IR: [cm^{-1}]: ν = 3466s, 3353s, 3188s (overall br feature), 2957w, 2926m 2856w, 1622s, 1429m, 1242s (sh), 1213s (sh), 1198vs, 1176(sh), 1163m (sh), 1131vs, 1080s, 1061s, 1040s, 1012m, 1004s, 934m, 888w, 847w, 764s, 758s, 726m, 697s. ^{1}H-NMR (D_2O): δ = 7.67 (m, 6H, **H**4,5); 8.13 (m, 6H, **H**3,6). *m*/*z* (−ve ES, 35v) 647 (100%, [LuL_2]$^-$), 679 (12.7, [LuL_2(MeOH)]$^-$), 711 (5.4, [$YL_2(MeOH)_2$]$^-$).

Synthesis of [H_7O_3][LaL_2] (14). Lanthanum(III) oxide (0.07 g, 0.21 mmol) and an excess of 1,2-benzenesulfonic acid (2.48 mmol) were reacted in water (10 mL) and the mixture was brought to reflux overnight. On work-up of the solution, **14** was obtained as crystals. A solution of the product in water had pH 1–2. Yield: 0.24 g (86%). $C_{12}H_{15}LaO_{15}S_4$ (666.39); C 21.62 (calc. 21.63); H 1.96 (2.27); La 21.57 (19.89)%. ν = IR: [cm^{-1}]: ν = 3505s (br), 1660s, 1623m, 1457m, 1418w, 1292w, 1278w, 1239s, 1175vs, 1160vs (sh), 1134vs, 1080m, 1065vs, 1039m, 1015m, 890w, 863w, 820w, 810w, 774m, 758m, 720w, 696s, 669m. ^{1}H-NMR (D_2O): δ = 7.66 (m, 4H, **H**4,5); 8.12 (m, 4H, **H**3,6). *m*/*z* (−ve ES, 35v) 611 (94.3%, [LaL_2]$^-$); (+ve ES, 35v) 375 (31.8%, [LaL]$^+$), 407 (55.4, [LaL(MeOH)]$^+$), 439 (43.9, [LaL$(MeOH)_2$]$^+$), 471 (51.6, [LaL$(MeOH)_3$]$^+$), 503 (100, [LaL$(MeOH)_4$]$^+$), 535 (5.7, [LaL$(MeOH)_5$]$^+$), 613 (8.3), 635 (4.5), 645(8.9), 677 (16.6), 709 (4.5).

Attempted synthesis of [La_2L_2L'], synthesis of [H_7O_3][LaL_2] (14). Lanthanum(III) 1,2-bezenesulfonate heptahydrate (0.50 g, 0.45 mmol) was dissolved in water (15 mL); perfluoroadipic acid (L′H) (0.13 g, 0.44 mmol) was added and the mixture was brought to reflux for 1 h. The solution was filtered and the filtrate evaporated to dryness leaving a white powdery product, which was then recrystallized from water, giving discrete crystals of **14**. A solution of the product dissolved in water indicated a pH value of 1–2. Yield: 0.54 (92%). ν = IR: [cm^{-1}]: ν = 3393s (vbr), 1667m, 1247vs, 1174vs, 1134vs, 1066vs, 1038s, 1010s, 968m, 926m, 769s, 760s, 691vs.

Attempted crystallization of [La_2L_3]; crystallization of [LaL(H_2O)$_7$]Cl·H_2O (15). From an attempt to crystallize **3**, a colourless crystal was obtained and shown to be **15** by X-ray crystallography. The bulk sample of **3** gave a negative test for Cl^-.

Structure determinations

Full spheres of CCD area-detector diffractometer data were measured (monochromatic Mo Kα radiation, λ = 0.7107$_3$ Å; *T ca.* 153 K) yielding $N_{t(otal)}$ reflections, these merging to N unique after 'empirical'/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ considered 'observed' and used in the full matrix least squares refinement, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x,y,z,U_{iso})_H$ being constrained at estimates, those for the water molecules being located in difference maps (see below). Conventional residuals, R, R_w on $|F|$ are cited at convergence (weights: $(\sigma^2(F) + 0.000n_w|F^2|)^{-1}$), computation using the Xtal 3.7 program system.[34] Pertinent results are given below and in the Tables and Figures, the latter showing 50% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms where shown having arbitrary radii of 0.1 Å.‡

Crystal/refinement data

[LnL(H_2O)$_6$]$_2$[L]·4H_2O. $C_{18}H_{44}Ln_2O_{34}S_6$, Ln = Y(**2**), Eu(**8**), Tb(**10**), Ho(**11**), Yb(**12**), Lu(**13**). These compounds are isomorphous, monoclinic, space group $P2_1/m$ (C^2_{2h}, No. 11), Z = 2. Refinement of a high quality data set for **8** on $|F^2|$, combined with refinement of $(x,y,z,U_{iso})_H$ (all H) provided a basis for the location of the (constrained) hydrogen atoms of the water molecules in the other structures, confirmed by difference map evidence. The determination of the Ln = Ho adduct (**11**) was carried out independently at a different location at 293 K (also true of **14**, at 123 K); compound **9** (Ln = Gd) is also isomorphous (a = 7.7312(7), b = 34.3793(5), c = 8.5272(8) Å, β = 111.261(6)°, V = 2112.2(5) Å^3 at 123 K.

Ln = Y, (2). M = 1174.7. a = 7.6984(4), b = 34.311(2), c = 8.5293(5) Å, β = 111.463(1)°, V = 2096.7(3) Å^3. ρ_{calcd} = 1.86$_0$ g cm^{-3}, Z = 2. $\mu_{(MoK\alpha)}$ = 3.2 mm^{-1}; crystal size: 0.25 × 0.19 × 0.12 mm; 'T'$_{min/max}$ = 0.66. $2\theta_{max}$ = 75°; N_t = 43 360, N = 11 104 (R_{int} = 0.030), N_o = 9289. R = 0.038, R_w = 0.050 (n_w = 6).

Ln = Eu, (8). M = 1300.8. a = 7.7426(5), b = 34.467(3), c = 8.5532(5) Å, β = 111.174(1)°, V = 2128.4(4) Å^3. ρ_{calcd} = 2.02$_9$ g cm^{-3}. $\mu_{(MoK\alpha)}$ = 3.3 mm^{-1}; crystal size: 0.40 × 0.17 × 0.14 mm; 'T'$_{min/max}$ = 0.70. $2\theta_{max}$ = 75°; N_t = 43 284, N = 11 278 (R_{int} = 0.030), N_o = 10 193. R = 0.030, R_w = 0.060 (n_w = 20).

Ln = Tb, (10). M = 1314.8. a = 7.7246(4), b = 34.366(2), c = 8.5388(4) Å, β = 111.327(1)°, V = 2111.5(3) Å^3. ρ_{calcd} = 2.06$_8$ g cm^{-3}. $\mu_{(MoK\alpha)}$ = 3.7 mm^{-1}; crystal size: 0.16 × 0.16 × 0.14 mm; 'T'$_{min/max}$ = 0.80. $2\theta_{max}$ = 75°; N_t = 43 562, N = 11 240 (R_{int} = 0.040), N_o = 9839. R = 0.035, R_w = 0.051 (n_w = 6).

Ln = Ho, (11). M = 1326.8. a = 7.6971(15), b = 34.283(7), c = 8.5201(17) Å, β = 111.43(3)°, V = 2092.9(7) Å^3. ρ_{calcd} = 2.10$_5$ g cm^{-3}. $\mu_{(MoK\alpha)}$ = 4.2 mm^{-1}; crystal size: 0.40 × 0.40 × 0.30 mm. $2\theta_{max}$ = 56°; N_t = 15 574, N = 4995 (R_{int} = 0.031), N_o = 4482 R = 0.023, R_w = 0.054.

Ln = Yb, (12). M = 1343.0. a = 7.6711(5), b = 34.174(3), c = 8.5082(5) Å, β = 111.555(1)°, V = 2074.5(2) Å^3. ρ_{calcd} = 2.15$_0$ g cm^{-3}. $\mu_{(MoK\alpha)}$ = 4.9 mm^{-1}; crystal size: 0.19 × 0.16 × 0.11 mm; 'T'$_{min/max}$ = 0.70. $2\theta_{max}$ = 75°; N_t = 42 551, N = 11 010 (R_{int} = 0.032), N_o = 10 603. R = 0.036, R_w = 0.065 (n_w = 5).

Ln = Lu, (13). M = 1346.9. a = 7.6640(7), b = 34.161(3), c = 8.5009(8) Å, β = 111.641(1)°, V = 2068.7(5) Å^3. ρ_{calcd} = 2.16$_2$ g cm^{-3}. $\mu_{(MoK\alpha)}$ = 5.2 mm^{-1}; crystal size: 0.38 × 0.34 × 0.30 mm; 'T'$_{min/max}$ = 0.65. $2\theta_{max}$ = 58°; N_t = 19 593, N = 5243 (R_{int} = 0.023), N_o = 5212. R = 0.025, R_w = 0.023 (n_w = 2).

[SmL(H_2O)$_6$][SmL$_2$(H_2O)$_4$]·'$8\frac{1}{4}H_2O$', (7). $C_{18}H_{48.5}O_{36.25}$;S_6Sm_2, M = 1338.2. Triclinic, space group $P\bar{1}$, a = 8.6666(5), b = 14.2258(6), c = 19.4202(7) Å, α = 103.476(1), β = 98.679(1)°, γ = 100.967(1)°, V = 2237.6(2) Å^3. ρ_{calcd} = 1.98$_6$ g cm^{-3}, Z = 2. $\mu_{(MoK\alpha)}$ = 3.0 mm^{-1}; crystal size: 0.28 × 0.22 × 0.14 mm; 'T'$_{min/max}$ = 0.72. $2\theta_{max}$ = 75°; N_t = 46 087, N = 22 980 (R_{int} = 0.021), N_o = 18 268. R = 0.025, R_w = 0.035 (n_w = 3).

Variata. Difference map residues O(4–15) were modelled as water molecule oxygen fragments (no associated hydrogen atoms located), site occupancies set at 0.5, 0.25.

[H_7O_3][LaL$_2$], (14). $C_{12}H_{15}LaO_{15}S_4$, M = 666.4. Triclinic, space group $P\bar{1}$, a = 9.750(2), b = 10.216(2), c = 11.647(2) Å, α = 64.72(3), β = 84.92(3), γ = 76.29(3)°, V = 1019.0(4) Å^3. ρ_{calcd} = 1.08$_6$ g cm^{-3}, Z = 1. $\mu_{(MoK\alpha)}$ = 1.29 mm^{-1}; crystal size: 0.20 × 0.16 × 0.18 mm; 'T'$_{min/max}$ = 0.95. $2\theta_{max}$ = 56°; N_t = 13 866, N = 4843 (R_{int} = 0.062), N_o = 4154. R = 0.029, R_w = 0.059 (n_w = 2).

[LaL(H_2O)$_7$]Cl·H_2O, (15). $C_6H_{20}ClLaO_{14}S_2$, M = 554.7. Triclinic, space group $P2_12_12_1$ (D^4_2, No. 19), a = 7.2560(5), b = 12.7526(8), c = 19.514(1) Å, V = 1805.7(3) Å^3. ρ_{calcd} = 2.04$_0$ g cm^{-3}, Z = 4. $\mu_{(MoK\alpha)}$ = 2.8 mm^{-1}; crystal size: 0.24 × 0.14 × 0.12 mm; 'T'$_{min/max}$ = 0.56. $2\theta_{max}$ = 75°; N_t = 36 963, N = 5287 (R_{int} = 0.041), N_o = 5105. R = 0.023, R_w = 0.030 (n_w = 5).

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