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Sm(III) complexation with α-amino acids X-ray crystal structure of $[Sm_2(Hala)_4(H_2O)_8](ClO_4)_4(Cl)_2$

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Abstract

Sm(III) coordination compounds are currently used as radiotherapeutic agents. Moreover, it is known that tumour cells show enhanced intake of α-amino acids ($H_n$aa). With this in mind, the study of samarium complexes with these ligands has obvious interest. In this work, potentiometric studies of Sm(III) in the presence of glycine, alanine, proline, tryptophane, valine, glutamic acid and cysteine have been carried out. Experiments were performed in aqueous solution ($[Sm^{3+}]$=5.0–60.0 mM) at 37°C and 0.15 M $NaClO_4$. Mono and dinuclear species were detected in the pH range 1.5–5.3. For higher pH values, $Sm(OH)_3$ competes with the formation of Sm complexes. In addition, Sm(III)–$H_n$aa complexes were isolated and characterized at solid state. The structure of $[Sm_2(Hala)_4(H_2O)_8](ClO_4)_4(Cl)_2$ is reported. In this complex, two Sm centres are joined by four μ-COO bridges. Four molecules of water complete the positions of each eight-coordinate Sm atom.

Keywords: Samarium; Amino acids; Alanine; Potentiometry; Crystal structure

1. Introduction

Coordination compounds of ^{153}Sm have been successfully used as radiotherapeutic agents. This is due to the excellent nuclear properties of this nuclide. ^{153}Sm (a β^- emitter) has a half life (46.27 h) short enough to deliver an appropriate dose in a relatively brief period. Besides, this radionuclide emits gamma rays that are nearly ideal for planar or SPECT scintigraphic imaging. This allows to follow the distribution of the radionuclide in vivo and to estimate dosimetry in patients [1–3]. For example, complexes of samarium (III) with phosphonate chelating agents, e.g. ^{153}Sm-EDTMP (EDTMP=ethylenediaminetetramethylene-phosphonic acid), have already been used to treat skeletal metastases [4]. These facts have promoted the development of the basic coordination chemistry of this 4f transition element.

On the other hand, the intake of α-amino acids ($H_n$aa) by abnormal cells is enhanced due to the special metabolism of tumour cells. So, it is possible to hypothesize that the captation of Sm(III) $H_n$aa complexes by tumour cells would be preferencial. However, suitable radiotherapeutic agents should be able to reach the target organ without any chemical modification, although they should be thermodynamically stable in the medium in which they will be used. In this sense, the stability constants of the possible coordination compounds of samarium under physiological conditions (37°C, 0.15 M ionic strength) should be evaluated. A few studies of coordination compounds of samarium with α-amino acids have been reported in various aqueous media [5–7] and different structures have been proposed, but results are somewhat confusing. The formation of solid $Sm(OH)_3$ as a side product must be considered when studying these systems. Very recently, $^*K_{s0}$ for this solid has been evaluated [8]. With this result, the complexation of Sm(III) with $H_n$aa (Hgly=glycine, Hala=alanine, Hpro=proline, Htrp=tryptophane, Hval=valine, H_2glu=glutamic acid and H_2cys=cysteine) is reported in this work. Experimental conditions have been chosen to resemble physiological medium (37°C, $NaClO_4$ 0.15 M) and the obtained results have been corrected, taking into account the hydrolysis reactions of samarium

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(III) (formation of $[Sm(OH)]^{2+}$ and $Sm(OH)_3(s)$) in such medium.

In order to go deeply in the structure of these complexes, $[Sm_2(Hgly)_6(H_2O)_4]^{6+}$ and $[Sm_2(Hala)_4(H_2O)_8]^{6+}$ were prepared and isolated in solid state. The crystal structure of the dimer $[Sm_2(Hala)_4(H_2O)_8](ClO_4)_4(Cl)_2$ is also reported.

2. Experimental

2.1. Materials

All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. All solutions were freed of carbon dioxide by Ar bubbling. The standard HCl and NaOH solutions were prepared from Merck standard ampoules. The Sm(III) stock solutions were prepared dissolving $SmCl_3 \cdot 6H_2O$ from Aldrich and standardised volumetrically by titration with the disodium salt of ethylenediaminetetraacetic acid (Na_2H_2edta from Sigma) at constant pH= 5, in the presence of sodium salt of methyl thymol blue as visual indicator.

2.2. Physical measurements

Infrared spectra were recorded on a Bomem FT-IR spectrophotometer as 1% KBr pellets. Elemental analyses were accomplished on a Carlo Erba EA1108.

2.3. Potentiometric measurements

Potentiometric titrations of acid stock solutions of samarium (III) chloride (concentrations ranging from ca. 5.0 to 60.0 mM) were carried out in presence of α-amino acids, using different metal to ligand molar ratios (1:1 to 1:10). The samarium concentration range was chosen taking into account the existent data, the experimental errors and the fact that for radiotherapeutic purposes, low concentrations are used (ca. 3 mM). These solutions were poured into a 50 ml titration cell and, after thermal equilibrium was reached, the hydrogen ion concentration was determined by a number of successive readings after each addition of small increments of standard 0.1 M NaOH solution. Similarly, free α-amino acids were titrated to determine the protonation constants. The e.m.f. were recorded by a Metrohm 713 pH Meter, using a glass electrode and a Ag–AgCl reference electrode. The ionic strength of the solutions was kept constant in the course of titrations by using solutions containing $NaClO_4$ 0.15 M and a relatively low concentration of metal ion. Presaturated argon (free of CO_2) was bubbled through the solutions during the course of titrations to eliminate the adverse effect of atmospheric carbon dioxide, and the temperature was kept at 37.0±0.1°C. The cell constants $E°$ and the liquid junction potentials were determined according to the methods of Sillén [9] and Liberti and Light [10]. Data were analysed using the HYPERQUAD program [11], and distribution species diagrams were produced using the HYSS program [12].

2.4. Synthesis of the complexes

2.4.1. $[Sm_2(Hgly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ **(1)**

To an aqueous solution (ca. 2 ml) of 20.6 mg of Hgly (0.274 mmo1), 100.0 mg of $SmCl_3 \cdot 6H_2O$ (0.274 mmol) and 77.0 mg of $NaClO_4 \cdot H_2O$ (0.274 mmo1) were added. pH was adjusted to 4.3 and the resulting solution was allowed to evaporate at room temperature. Upon slow evaporation (and after white crystals of sodium perchlorate were separated) pale yellow crystals of **1** were obtained. Yield: 20%. IR spectrum (v, cm^{-1}): 1613 (s), 1498 (m), 1464 (m), 1417 (m), 1334 (s), 1145 (vs), 1116 (vs), 1087 (vs), 916 (m), 902 (m) 627 (s), 524 (m), 508 (m). Anal. Calc. for $Sm_2C_{12}H_{48}O_{45}N_6Cl_6$: C, 9.5; H, 3.2; N, 5.6. Found: C, 9.7; H, 2.6; N, 5.4.

2.4.1.1. $[Sm_2(Hala)_4(H_2O)_8](ClO_4)_4(Cl)_2$ **(2)**

To an aqueous solution (ca. 2 ml) of 24.4 mg of Hala (0.274 mmo1), 100.0 mg of $SmCl_3 \cdot 6H_2O$ (0.274 mmo1) and 120.1 mg of $NaClO_4 \cdot H_2O$ (0.822 mmo1) were added. pH was adjusted to 4.0 and the resulting solution was allowed to evaporate at room temperature. Within a month and after white crystals of sodium perchlorate were separated, pale yellow crystals of **2** were obtained. Yield: 20%. IR spectrum (v, cm^{-1}): 1683 (s), 1636 (m), 1490 (m), 1432 (m), 1345 (m), 1145 (vs), 1113 (vs), 1089 (vs), 628 (s), 560 (m). Anal. Calc. for $Sm_2C_{12}H_{44}O_{32}N_4Cl_6$: C, 11.3; H, 3.5; N, 4.4. Found: C, 12.2; H, 3.7; N, 4.7.

2.5. Crystallographic measurements and structure determinations

Pale yellow prismatic crystals of **2** were obtained in the triclinic, non-centrosymmetric space group $P1$. The cell parameters were refined with 25 centered intensities in the θ range 45.28–49.10°. From the 4582 reflections collected in the range: $-7 \le h \le 13$, $-13 \le k \le 12$, $-13 \le l \le 12$, 3982 were unique ($R_{int} = 0.1063$) while 3852 reflections were observed [$I > 2\sigma(I)$].

X-ray data collection was performed at room temperature (298(2) K) on a Rigaku AFC-7S diffractometer [13] using monochromated (graphite) MoKα radiation (λ= 0.7107 Å) in the ω–2θ scan mode in a θ range 2.18–25.73°. During the data collection the intensity of three standard reflections was monitored every 150 measurements to correct for intensity decay. Lorentz, polarization and absorption corrections were applied. The structure of **2** was solved by direct methods locating most non-hydrogen atoms. The structures were completed by successive difference Fourier maps. Refinement was anisotropic for

Table 1
Ionization constants of α-amino acids at 37°C and $I=0.15$ M $NaClO_4$

H_naa	Concentration range (mM)	Titrations	pH range	Exp. points	σ	log β_{11}	log β_{1-1}	log β_{1-2}
Hgly	14.0–22.0	2	2.1–9.7	110	1.8	2.19±0.02	−9.15±0.02	–
Hala	16.0–23.0	2	2.2–9.5	161	0.9	2.319±0.004	−9.361±0.006	–
Hpro	10.0–17.0	2	1.5–10.2	97	0.9	2.11±0.01	−10.218±0.008	–
H_2glu	9.7–19.0	2	2.1–9.7	202	1.3	2.160±0.006	−4.130±0.003	−13.339±0.004
Htrp	10.0–22.0	3	2.2–9.4	155	0.7	2.238±0.003	−8.949±0.002	–
Hval	12.0–19.0	2	2.5–9.5	104	0.9	2.250±0.006	−9.131±0.003	–
H_2cys	3.8–7.9	3	2.0–9.7	51	0.6	1.84±0.01	−7.864±0.003	−17.797±0.006

all non-hydrogen atoms except for two oxygen atoms belonging to one of the four perchlorates present in this structure. All hydrogen atoms were calculated at idealized positions and with fixed distances (0.98 Å for $C_{(tertiary)}$–H, 0.96 Å for $C_{(primary)}$–H, and 0.96 Å for $N_{(Hala)}$–H) and refined with an isotropic displacement parameter related to the equivalent isotropic displacement parameter of the atom to which it is bonded. The H atoms from the water molecules attached to samarium were neither found nor calculated. Structure determination was achieved using SHELXS [14] and refinement was done using SHELXL programs included in the SHELX-97 [15] package. Geometric calculations and structural checking were performed with the PLATON-98 program [16]. The ZORTEP program [17] was used to plot the drawings. Absorption correction was performed by φ-scan [13] and extinction correction was applied.

3. Results and discussion

The protonation constants found for the studied α-amino acids are depicted in Table 1. Depending on the amino acid, the involved processes are:

$$Haa + H^+ \rightleftarrows H_2aa^+ \qquad \beta_{11}$$
$$Haa \rightleftarrows aa^- + H^+ \qquad \beta_{1-1}$$
$$H_2aa \rightleftarrows aa^{2-} + 2H^+ \qquad \beta_{1-2}$$

The results are in line with those previously reported [18].

The formation of Sm(III) complexes with α-amino acids in aqueous solution is only possible at those pH values in which $Sm(OH)_3$ does not compete. Beyond pH 5, the precipitation of the hydroxide is a serious competitive product.

In order to study these Sm(III)–$H_n$aa systems, previous hydrolysis studies [8] were taken into account, in particular the formation of $[Sm(OH)]^{2+}$ ($\log {}^*K_1 = -0.83\pm0.02$). The obtained potentiometric results, together with the experimental conditions, are depicted in Table 2. Formation constants correspond to the equilibrium quotients of the processes:

$$Sm^{3+} + H_naa \rightleftarrows [Sm(H_naa)]^{3+} \qquad \beta_{110}$$
$$Sm^{3+} + 2H_naa \rightleftarrows [Sm(H_naa)_2]^{3+} \qquad \beta_{120}$$
$$Sm^{3+} + 2H_naa \rightleftarrows [Sm(H_{n-1}aa)(H_naa)]^{2+} + H^+ \qquad \beta_{12-1}$$
$$Sm^{3+} + 2H_naa \rightleftarrows [Sm(H_{n-1}aa)_2]^{+} + 2H^+ \qquad \beta_{12-2}$$
$$Sm^{3+} + 3H_naa \rightleftarrows [Sm(H_{n-1}aa)(H_naa)_2]^{2+} + H^+ \qquad \beta_{13-1}$$
$$2Sm^{3+} + 4H_naa \rightleftarrows [Sm_2(H_naa)_4]^{6+} \qquad \beta_{240}$$
$$2Sm^{3+} + 6H_naa \rightleftarrows [Sm_2(H_naa)_6]^{6+} \qquad \beta_{260}$$

The analysis of the potentiometric experimental data show the formation of both, mononuclear and dinuclear species. Previous solution studies [5–7] only reported the existence of mononuclear complexes with different stoichiometries, mainly with molar ratio 1:1. Dinuclear species in which an

Table 2
Stability constants for α-amino acids with Sm(III) at 37°C and $I=0.15$ M $NaClO_4$

H_naa	Ligand to metal molar ratio	Titrations	pH range	Exp. points	σ	log β_{110}	log β_{120}	log β_{12-1}	log β_{12-2}	log β_{13-1}	log β_{240}	log β_{260}
Hgly	1–3	4	2.2–4.3	206	3.1	1.60±0.09	–	–	–	1.36±0.05	–	13.3±0.1
Hala	1–4	3	2.3–4.2	247	2.6	–	1.67±0.04	–	–	–	5.02±0.05	–
Hpro	1–4	4	1.5–4.3	268	0.8	2.95±0.02	3.71±0.02	–	–	–	–	–
Htrp	1–3	3	1.5–3.8	165	1.0	1.72±0.05	–	–	–	0.67±0.12	–	–
Hval	1–3	3	1.4–4.2	162	0.6	1.64±0.04	–	–	–	0.67±0.10	–	–
H_2glu	1–4	3	1.8–5.3	256	0.8	–	–	0.48±0.01	−3.40±0.01	–	10.05±0.05	–
H_2cys	1–10	5	1.6–4.3	228	0.6	1.443±0.001	–	–	–	−1.71±0.01	–	–

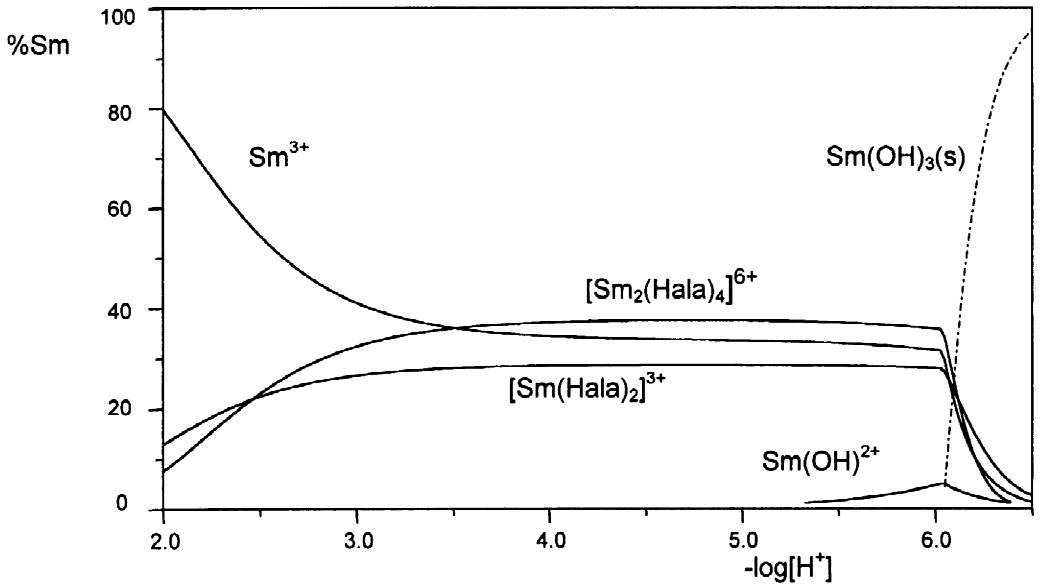

Fig. 1. Species distribution diagram (37°C, 0.15 M $NaClO_4$) for the system Sm–Hala. Ligand: metal ratio 4:1 and $C_M = 50$ mM.

α-amino acid acts as a bridge between lanthanide centers are well known and characterized [19,20]. However, these species have only been reported in solid state. Our results show that dinuclear species also exist in solution, at least under the studied conditions. For glycine and alanine, $[Sm_2(Hala)_4]^{6+}$ and $[Sm_2(Hgly)_6]^{6+}$ species were detected. For the remaining systems, mononuclear complexes with molar ratios 1:1 and 1:3 were also found. It is worth noting that most species contain the amino acid in the

Table 3
Crystal data and structural refinement parameters for structure **2**

Chemical formula	$C_{12}H_{44}O_{32}N_4Sm_2Cl_6$
Formula weight	1269.91
Space group	*P*1
a (Å)	10.822(3)
b (Å)	11.190(3)
c (Å)	10.744(3)
a (°)	109.88(2)
b (°)	101.85(3)
c (°)	112.39(2)
V (Å^3)	1043.9(5)
Z	1
D_{calcd} (g·cm^{-3})	2.020
μ (mm^{-1})	3.271
F(000)	626.0
Crystal dimensions (mm)	0.15×0.20×0.30
Transmission factors range	0.4403–0.6396
θ range (°)	2.18–25.73
Data collected	4582
Number of observed data [$I>2\sigma I$]	3852
Absolute structure parameter [*x*]	0.08(3)
R_1 [a]	0.0532
wR_2 [b]	0.1405
s_1 [c]	0.1067
s_2 [c]	3.7634

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_c|$.
[b] $wR_2 = \{\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2\}^{1/2}$.
[c] $w = 1/[\sigma^2(F_0^2)+(s_1^*P)^2+s_2^*P]$; $P(F_0^2+2F_c^2)/3$.

Table 4
Relevant bond lengths (Å) and angles (°) for **2**

Bond lengths			
Sm1 O11	2.329(14)	Sm2 O21	2.367(16)
Sm1 O12	2.360(13)	Sm2 O22	2.329(14)
Sm1 O13	2.354(11)	Sm2 O23	2.439(14)
Sm1 O14	2.342(10)	Sm2 O24	2.396(15)
Sm1 O15	2.573(14)	Sm2 O25	2.510(16)
Sm1 O16	2.481(16)	Sm2 O26	2.441(14)
Sm1 O17	2.505(14)	Sm2 O27	2.416(11)
Sm1 O18	2.479(14)	Sm2 O28	2.430(17)
Bond angles			
O11 Sm1 O13	123.6(5)	O21 Sm2 O23	121.6(5)
O14 Sm1 O13	78.6(5)	O24 Sm2 O23	73.7(5)
O11 Sm1 O12	78.6(5)	O21 Sm2 O22	73.9(5)
O14 Sm1 O12	124.5(5)	O24 Sm2 O22	119.6(5)
O13 Sm1 O12	80.1(5)	O23 Sm2 O22	79.2(5)
O11 Sm1 O18	140.0(5)	O21 Sm2 O28	83.5(5)
O14 Sm1 O18	86.1(5)	O24 Sm2 O28	145.8(6)
O13 Sm1 O18	82.3(5)	O23 Sm2 O28	140.3(5)
O12 Sm1 O18	140.0(5)	O22 Sm2 O28	79.7(5)
O11 Sm1 O16	74.9(6)	O21 Sm2 O26	144.1(5)
O14 Sm1 O16	76.2(6)	O24 Sm2 O26	137.7(5)
O13 Sm1 O16	141.5(6)	O23 Sm2 O26	72.4(5)
O12 Sm1 O16	138.4(6)	O22 Sm2 O26	77.5(5)
O18 Sm1 O16	67.4(6)	O28 Sm2 O26	70.5(5)
O11 Sm1 O17	86.7(5)	O21 Sm2 O27	138.1(5)
O14 Sm1 O17	143.5(5)	O24 Sm2 O27	74.7(5)
O13 Sm1 O17	137.4(S)	O23 Sm2 O27	77.9(5)
O12 Sm1 O17	77.4(5)	O22 Sm2 O27	147.7(5)
O18 Sm1 O17	92.3(5)	O28 Sm2 O27	104.5(5)
O16 Sm1 O17	69.6(5)	O26 Sm2 O27	74.1(5)
O11 Sm1 O15	146.0(6)	O21 Sm2 O25	70.7(5)
O14 Sm1 O15	140.7(6)	O24 Sm2 O25	74.0(6)
O13 Sm1 O15	70.2(6)	O23 Sm2 O25	140.8(5)
O12 Sm1 O15	73.4(6)	O22 Sm2 O25	137.2(5)
O18 Sm1 O15	66.8(6)	O28 Sm2 O25	73.2(6)
O16 Sm1 O15	115.1(6)	O26 Sm2 O25	121.5(5)
O17 Sm1 O15	68.8(5)	O27 Sm2 O25	72.6(5)
O11 Sm1 O14	72.1(5)	O21 Sm2 O24	76.5(5)

zwitterionic form; this would indicate that coordination occurs through the carboxylate groups while the amino nitrogens remain protonated and uncoordinated. Anionic ligands become significant for H_2glu and H_2cys, i.e. those α-amino acids which possess a more acidic proton.

Fig. 1 shows the species distribution diagram for the system Sm(III)–Hala. As can be seen, at low pH values, $[Sm_2(Hala)_4]^{6+}$ and $[Sm(Hala)_2]^{3+}$ are present in solution. As the pH is raised, a small amount of $[Sm(OH)]^{2+}$ is present and finally $Sm(OH)_3$ precipitates.

The isolation of glycine and alanine complexes in solid state, confirms the presence of dinuclear species. As revealed by elemental analyses, their formulas were consistent with potentiometric results. Each complex shows a remarkable difference between the two COO stretching vibrations (symmetric and antisymetric). In both complexes they are nearly 200 cm^{-1} apart. The shifts are close to those of the free ion value (197 and 185 cm^{-1} for Hgly and Hala, respectively [21]). This agrees with the trend for complexes with bridging amino acids ([22] Table 3).

The structure of the solids were confirmed by crystallographic analyses. Complex **1** proved to be $[Sm_2(Hgly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ which had been previously reported by other authors [23]. It was also possible to obtain single crystals of compound **2**. Relevant distances and angles are shown in Table 4. The crystal structure of the $[Sm_2(Hala)_4(H_2O)_8](ClO_4)_4Cl_2$ complex consists of dimeric units (see Fig. 2), one per unit cell. These units have four carboxylate groups bridging two eight coordinate samarium atoms (Sm–O distances between 2.329(14) and 2.439(14) Å) and four water molecules (Sm–O distances between 2.416(11) and 2.573(14) Å) that complete their coordination sphere, resulting in a cubic antiprism geometry. These distances are shorter than those of the complex $[Sm_2(\beta\text{-Hala})_6(H_2O)_4](ClO_4)_6 \cdot H_2O$ (2.433 and 2.579 Å, respectively) [20]. On the other hand, the distances are longer than those of the analogous $[Er_2(Hala)_4(H_2O)_8](ClO_4)_6$ (2.285 and 2.392 Å, respectively) [19]. This fact reflects the smaller size of Er^{3+}, due to the lanthanide contraction.

Since the alanine molecule was optically pure the structure should be non-centrosymmetric as was found. However, it presents pseudo-symmetry relating the two mononuclear units, where the symmetry is broken due to the terminal alanine groups that contain the chiral carbon atoms (C2, C4, C6 and C8) which have an absolute

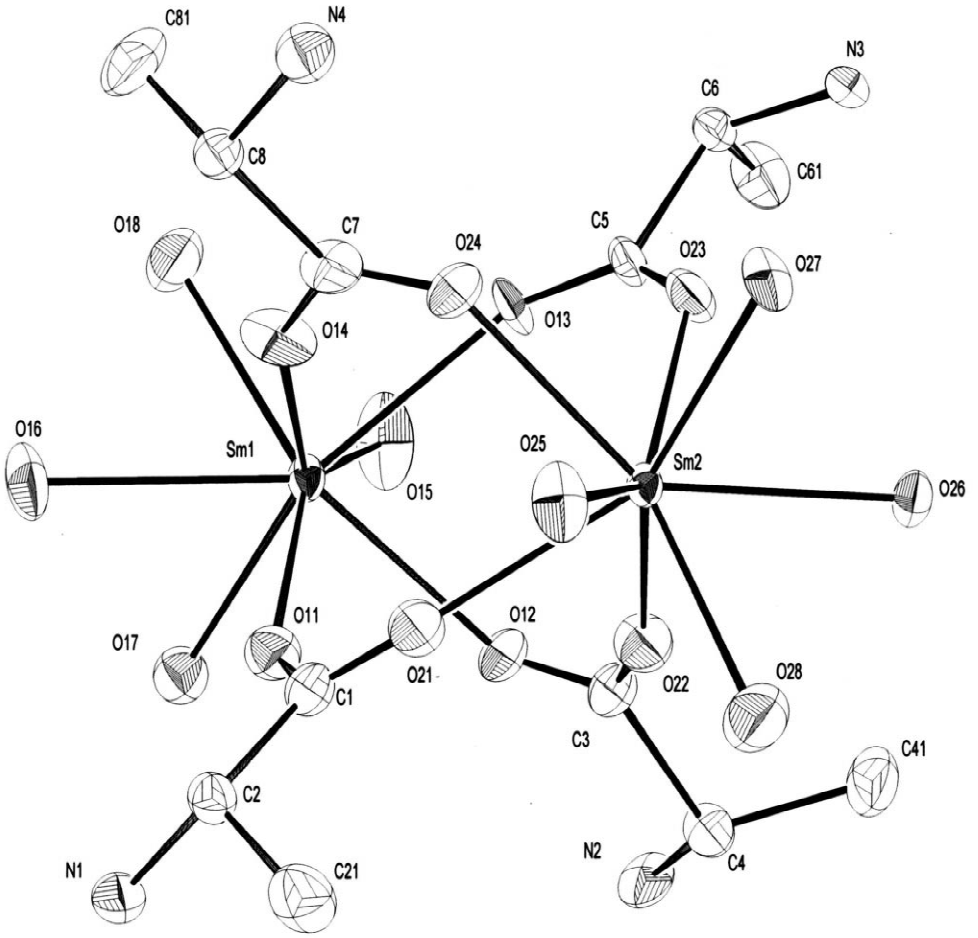

Fig. 2. ZORTEP view of the binuclear cationic complex $[Sm_2(Hala)_4(H_2O)_8](ClO_4)_4(Cl)_2$ (with labelling scheme). Ellipsoids are drawn with a probability of 30% and the H atoms were excluded for clarity.

structure *S*. The coordination planes where the opposite alanines are located (Sm2–O21ClO11–Sm1–O13C5O23–Sm2 and Sm2–O22C3O12–Sm1–O14C7O24–Sm2) are perpendicular within experimental error (89.9(1)°). The packing is directed by hydrogen bonds involving carboxylic oxygen atoms, perchlorate anions and amine groups. Although no H water atoms could be located the distances between the O atoms in the water molecules and other groups (amines, chlorides, oxygen atoms belonging to perchlorate anions and other water molecules) suggest the existence of hydrogen bonds involving these H.

4. Supplementary material

Complete listings of atomic coordinates, anisotropic thermal parameters, complete bond distances and angles, hydrogen coordinates, as well as a listing of calculated and observed structure factors are available from the Cambridge Crystallographic Data Centre, quoting the deposition number 147103. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.aaac.uk).

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