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1. Introduction

Colloidal systems involving long chain anionic amphiphiles and trivalent metal ions have applications in detergency,¹ wastewater treatment,^{2,3} gel formation and development of thickeners and dispersants,^{4,5} catalysis,^{6,7} analytical chemistry,⁸ froth flotation for metal ion recovery,⁹ and contrast agents for magnetic resonance imaging.¹⁰ They form ordered nanostructures through self-assembly which also have considerable potential in materials science, including tunable UV/visible light emitters,¹¹ templated synthesis of mesoporous materials,^{12,13} production of lanthanide-based glasses for photonic applications,^{14,15} preparation of nanoparticles,¹⁶ and formation of metal–organic frameworks (MOFs).¹⁷ They are also

Structural characterization of solid trivalent metal dodecyl sulfates: from aqueous solution to lamellar superstructures[†]

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Metal dodecyl sulfates of trivalent aluminium, chromium, lanthanum and gadolinium were prepared by addition of the corresponding salts to aqueous solutions of sodium dodecyl sulfate at the natural pH (*ca.* 6). Using X-ray diffraction, FT-IR and NMR spectroscopy, DSC, thermogravimetry and polarizing light thermomicroscopy it is shown that metal dodecyl sulfates are formed with lamellar structures. These have different degrees of hydration, which depend upon the metal ion. In some cases there is evidence for coexistence of different lamellar phases. The metal is strongly bound electrostatically to the sulfate group, and although the alkyl chain is in an extended conformation, there are suggestions of local disordering of the methylene groups adjacent to the anionic head group. SEM with an EDS probe on the trivalent metal complexes shows a 1 : 3 ratio at the surface identical to the bulk structure. Studies by SEM and AFM provide evidence of periodicity, which is likely to be induced by the lamellar, layered structures. Differences are observed in the thermal behavior, which appear to reflect both the coordination behavior of the metal ion and the degree of hydration.

relevant for the development of layered hydroxide composite systems for a variety of materials applications.^{18,19}

The addition of trivalent metal salts to sodium dodecyl sulfate (SDS) in aqueous solutions almost invariably leads to precipitation, due to formation of the trivalent metal dodecyl sulfates. However, as has been discussed elsewhere,^{20–25} the metal–dodecyl sulfate interaction depends on the nature and concentration of the metal ion and also on the precipitation conditions (pH, temperature, *etc.*).

The synthesis of metal dodecyl sulfates, such as $Cu(DS)_2$ and $Zn(DS)_2$, was first reported by Matuura *et al.* who used the addition of SDS to a solution of the metal nitrate or chloride.^{26–28} Firouzabadi *et al.* synthesized $Al(DS)_3 \cdot H_2O$ and investigated its successful application in the Michael addition of indoles and pyrrole to α,β -unsaturated electron-deficient compounds in aqueous media at room temperature. In this study, they found that the catalytic activity of $Al(DS)_3 \cdot 3H_2O$ is greater than that of $Sc(DS)_3$.²⁹ $Al(DS)_3 \cdot 3H_2O$ was also employed efficiently as a catalyst for the conversion of epoxides into thiiranes with thiourea in water at room temperature in excellent yields.³⁰

These compounds are frequently referred in literature as Lewis acid-surfactant-combined catalysts.^{30–32} The development and use of new environmentally-friendly Lewis acid catalysts is increasing due to the introduction of increasingly restrictive environmental regulations applied to industrial processes. When conventional Lewis acid catalysts are used,

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^d*Faculty of Pharmacy, University of Coimbra, 3004-295 Coimbra, Portugal* † Electronic supplementary information (ESI) available: XRD patterns of the metal dodecyl sulfate complexes, EDS spectrum of all M(DS)₃ complexes, TGA and DTG curves of the metal dodecyl sulfate complexes M(DS)₃ in the high temperature region, FT-IR spectra of the metal dodecyl sulfate complexes M(DS)_n: in the vOH, vC–C and sulfate regions, and discussion of interpretation of FT-IR spectra for the sulfate group vibrations. See DOI: 10.1039/c2ra21906a

an additional step is often required to remove the acid–base adduct formed between products and catalyst.³³ This process usually leads to catalyst degradation and generation of chemical wastes.^{33,34} In contrast, "green" Lewis acid catalysts are not corrosive, do not require neutralization steps for separation, are more selective and can be reused.³³

Metal centers combined with surfactant molecules have been proposed as powerful catalysts for several other reactions: aldol condensation, regioselective ring opening, Michael addition, Diels–Alder, and esterification;^{30,32,34–36} furthermore, these materials are capable of performing organic reactions in water.

In addition, metal-surfactant compounds can be used as socalled organic-inorganic hybrid nanocomposites. The development of such new types of porous hybrid materials allows the design of composites with different guests.³⁷ Mesoporous materials can also be synthesized in the presence of surfactants; here the surfactant acts as a template for the formation of the mesoporous network, with the length of the alkyl chain determining the size of the pores.^{14,17} These materials show suitable morphologies for applications in optical, electronic, and sensing devices, as well as for separation, due, in particular, to their versatility as coatings on various substrates and commercial supports such as optical fibers.^{14,15,17,37} In general, such trivalent metal hybrid materials containing, for example, lanthanides, have improved mechanical properties and better processability than the pure molecular complexes, in addition to showing improvements in thermal stability and luminescence output.14,15

A detailed understanding of structural aspects of metal surfactant systems is important for many of these applications. We report the structural, thermal and spectroscopic characterization of dodecyl sulfates of trivalent metals. Four model metal ions have been chosen for their different characteristics: Al³⁺, Cr³⁺, La³⁺ and Gd³⁺. The first two have environmental importance, in addition to showing different coordination behavior. Although Al³⁺ and Cr³⁺ are normally both hexacoordinated, differences are seen in substitution of their water molecules, with aluminum(III) being kinetically labile, while chromium(III) is inert, only undergoing very slow water substitution reactions.38 With lanthanum(III) and gadolinium(III), both show a wide range of useful physical properties, including luminescent and magnetic characteristics.³⁹ In addition, because of the fairly uniform complexation behavior of this group of elements, once the characterization of one lanthanide surfactant system has been made, its behavior can readily be extended to other trivalent lanthanides. However, subtle differences exist along the series of the lanthanide ions, sometimes leading to a decrease in coordination number,⁴⁰ and it is anticipated that the behavior of La³⁺ and Gd³⁺ may be different, and may reflect the behavior of lanthanide ions at the beginning and end of the series.

The structural and physical-chemical characterization of the metal dodecyl sulfates has been carried out by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized light thermal microscopy (PLTM), spectroscopic analysis (FT-IR, ¹H and ¹³C NMR) and X-ray diffraction (XRD). In addition, morphological studies have been performed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM studies of the trivalent metal complexes have been complemented by energy-dispersive X-ray spectroscopy (EDS).

2. Experimental

2.1 Materials

Aluminum(III) nitrate nonahydrate (Al(NO₃)₃·9H₂O, 98.0%), chromium(III) nitrate nonahydrate (Cr(NO₃)₃·9H₂O, 99.0%), lanthanum(III) nitrate hexahydrate (La(NO₃)₃·6H₂O, 99.999%), gadolinium(III) perchlorate (Gd(ClO₄)₃, 40 wt % solution in water), and sodium dodecyl sulfate (CH₃(CH₂)₁₁OSO₃Na, SDS, \geq 98%) were purchased from Sigma-Aldrich. These reagents were used as received, and all solutions were prepared using Millipore-Q water. All experiments were carried out at 25 °C unless otherwise stated.

2.2 Preparation of metal dodecyl sulfates

Recently we reported that DS⁻ ions interact at the natural pH in water with trivalent metal ions $(M^{3+} = Al^{3+}, Cr^{3+}, Gd^{3+})$ and La^{3+}) to form solids in a 3 : 1 stoichiometry, ^{21,22} corresponding to charge neutralization. However, in contrast to what is expected for metal tri(dodecyl sulfate)s, (M(DS)₃), it has been found that the maximum interaction stoichiometry occurs at around 4 : 1, suggesting a change in the solid structure which allows the best packing of DS⁻ ions around the metal ions.²¹ Based on these observations, the following experimental procedure was adopted: a certain volume of 0.1 M SDS solution was added, under continuous stirring, to a 1 mM trivalent metal salt solution until the concentration ratio r (where $r = [SDS]/[M^{3+}]$) of 4 was attained, and then left stirring for at least 6 h. The resulting precipitate was collected, centrifuged, washed with water and then lyophilized for about 24 h. All metal(III) solids were prepared in the same manner from their respective salts.

2.3 Experimental methods

¹H and ¹³C NMR spectra were acquired in deuterated methanol (99.80%) on a Varian 600 MHz spectrometer using a 5 mm broadband probe. Typical acquisition parameters for ¹H NMR spectra included a 45° radiofrequency observation pulse and 32 000 points covering a spectral width of 8 kHz. For ¹³C NMR spectra 132 000 points were acquired for resolving the 35 kHz spectral widths; a sequence with a 45° radiofrequency pulse and an interpulse duration of 3 s were used to allow full relaxation of aliphatic carbons.

XRD patterns of the dried (lyophilized) samples were recorded at room temperature using a Philips PW-170 diffractometer. The samples were exposed to monochromatic Cu-K α radiation (λ = 1.5418 Å, 50 kV, 40 mA) over the 2 θ range between 20 and 70° in steps of 0.02°.

High Resolution Scanning Electronic Microscopy (HR-SEM) micrographs were obtained using a FEI Quanta 400FEG/Edax Genesis X4M scanning electron microscope. Elemental analysis on microscopic sections of each $M(DS)_3$ sample was performed by Energy Dispersive Spectroscopy (EDS). SEM images were obtained at high or low vacuum, depending on sample charging effects, and in the secondary electrons mode or backscattered electrons mode.

AFM images were recorded with a Veeco Metrology Multimode/Nanoscope IVA equipment (CEMUP-Porto contract REEQ/1062/CTM/2005), in tapping mode using a super sharp silicon tip, curvature radius 10 nm, and frequency resonance equal to ≈ 300 kHz. Flattening and elimination of line noise tools and a Lowpass filter provided by the WSXM software⁴¹ were used to improve the quality of the images.

For the DSC measurements a dried (lyophilized) sample with a mass of approximately 8 mg was placed in a 50 μ l perforated aluminium pan and the thermogram was recorded using a Perkin Elmer Pyris1 Differential Scanning Calorimeter. An empty pan was employed as reference. The sample was heated at 10 °C min⁻¹ from 0 to 190 °C using dried high purity nitrogen as purge gas supplied at a constant flow rate of 20 mL min⁻¹. All samples for each material were collected from the same precipitate.

For the TGA measurements dried samples were transferred to open platinum crucibles and analyzed from room temperature to 900 °C using a TA Q50 Thermogravimetric Analyser at a heating rate of 10 °C min⁻¹ using dried high purity nitrogen as purge gas supplied at a constant flow rate (40 mL min⁻¹ and 60 mL min⁻¹ in the balance and sample chamber, respectively).

The dried solids were characterized by PLTM using a hot stage Linkam system (model DSC600) equipped with a Leica DMRB microscope and a Sony CCD-IRIS/RGB video camera. Real Time Video Measurement System software by Linkam was used for image analysis. The images were obtained by combined use of polarized light and wave compensators, using a $200 \times$ magnification.

The FT-IR spectra were acquired at room temperature in transmission mode using a Nicolet 6700 FT-IR spectrometer from Thermo Scientific. The spectra were collected over the 4000–400 cm⁻¹ range by averaging 64 scans at a spectral resolution of 2 cm⁻¹. Solid dried samples were finely ground, mixed with dried potassium bromide (Merck, spectroscopic grade) and pressed into pellets.

3. Results and discussion

Initial characterization of the M(DS)₃ complexes was carried out in solution using NMR spectroscopy. ¹H and ¹³C NMR spectra of SDS dissolved in CD3OD were obtained and compared with those acquired for each of the complexes of the trivalent metal ions. The SDS ¹H NMR spectrum (Fig. 1(a)) showed chemical shifts at δ = 4.02 (i), 1.70 (ii), 1.44 (iii), 1.33 (iv) and 0.94 (v) ppm. ¹H peak assignments are given in the scheme in Fig. 1, and are similar to those reported for other dodecyl compounds.^{6,29,31,42} The peak at 3.35 ppm is from vestigial CHD₂OD. The ¹³C NMR spectrum of SDS (Fig. 1(b)) presents peaks at δ = 69.43, 33.34, 31.06, 31.03, 30.99, 30.97, 30.74, 30.67, 27.18, 24.00 and 14.72 ppm. The resonances α, β and γ (Fig. 1(b)) indicate the methylene groups immediately following to the sulfate in the dodecyl sulfate aliphatic chain. The intense peak at 49.30 ppm is from CD₃OD. ¹H and ¹³C NMR spectra of each of the complexes are also shown in the



Fig. 1 ¹H (a) and ¹³C (b) NMR spectra of metal dodecyl sulfate complexes $M(DS)_n$ in CD_3OD .

figure and are similar to spectra reported for other metal dodecyl complexes. 6,31

The complexation with the M^{3^+} ions induced changes in both chemical shifts and linewidths. A complete analysis of those changes was made and revealed that the noteworthy alterations were those associated with the methylenic groups in close proximity to the sulfate group. As expected, the paramagnetic Cr^{3^+} and Gd^{3^+} ions induced significant broadening in both ¹H and ¹³C resonances. All metals cause a small downfield shift of the proton resonance at ~4.0 ppm, assigned to the methylene group adjacent to the sulfate group (i), which is caused by the trivalent metal ions binding the surfactant head group. The largest shift is seen for La(DS)₃ ($\Delta\delta$ of 0.09 ppm) and the largest broadening for the same



Fig. 2 XRD patterns of the metal dodecyl sulfate complexes $M(DS)_n$ in the low-q region.

methylenic group in the $Gd(DS)_3$ complex, consistent with the large paramagnetic character of this metal ion.

Changes in ¹³C chemical shifts are observed for all complexes, but are less pronounced for the $Al(DS)_3$ complex. In terms of relaxation, significant increases in relaxation rates (as derived from ¹³C resonance linewidths) can be seen for the methylene group attached to the sulfate (α from Fig. 1(b)) with $\Delta \delta = 0.9, 0.2, 0.3$ and 2.7 ppm for La(DS)₃, Al(DS)₃, Cr(DS)₃ and $Gd(DS)_3$ complexes, respectively. Although less pronounced, it was also possible to observe some changes in both chemical shifts and linewidths in the signals of the two methylene groups at 30 and ~27 ppm (β and γ from Fig. 1(b)), suggesting that these are the two CH2 groups immediately following the α -methylene in the dodecyl sulfate aliphatic chain. It is worth noting that only one set of DS⁻ resonances is observed both for ¹H and ¹³C NMR spectra, showing that all coordinated DS⁻ ions have the same chemical and magnetic environments in solution. In addition, the fact that relatively sharp resonances are seen for the terminal methyl and associated methylene groups in the DS complex with the paramagnetic Gd³⁺ ion indicates that the alkyl chains of the DS⁻ ligands are extended, outside the volume of paramagnetic influence of this lanthanide. This NMR analysis clearly demonstrates that the chemical and magnetic environments of the proton and carbon nuclei in close proximity to the sulfate group are the most affected and such effects differ depending on the M3+ ion.

The XRD patterns of the solid $M(DS)_3$ compounds are shown in Fig. 2. The solids show a reasonable degree of crystallinity, as indicated by the relatively sharp peaks observed in the low q region ($q = 4\pi \sin \theta/\lambda$ where 2θ is the scattering angle and λ is the wavelength) where at least three (001) reflections are distinctly seen. At $q < 8 \text{ nm}^{-1}$ the XRD patterns of SDS, Al(DS)₃ and Cr(DS)₃ (red, blue and green vertical continuous lines in Fig. 2(a), respectively) and SDS, La(DS)₃, and Gd(DS)₃ (red, blue and green vertical continuous lines in Fig. 2(b), respectively) are compared. All the patterns exhibit a series of peaks which correspond to the k^{th} order reflections of a lamellar structure with an interlamellar spacing d_1 (where $d_1 = k2\pi/q_k$). The d_1 values, listed in Table 1, calculated for all the complexes using the position of

 Table 1 Characteristic distances (in nm) of the metal dodecyl sulfate complexes and ionic radii (in nm) of the corresponding cations

+ 40
390^{a} 020^{b}
535
615
938
032

^a Tetrahedral coordination. ^b Octahedral coordination.



Fig. 3 Ionic radii dependence of the lamellar spacing of the main bilayer structure (d_1 , filled symbols) and of the thickness of the water layer (d_W , open symbols) of the metal dodecyl sulfate complexes $M(DS)_n$. The lines drawn are just guides for the eyes.

the most intense diffraction peak, are characteristic of lamellar arrangements.^{6,43} These data are in agreement with those obtained for other M(DS)₃ compounds incorporating lanthanide ions (M = Nd, Yb, Gd and Ce).^{6,44} The d_1 values correspond to the successive (001) reflections through planes of atoms of a lamellar bilayer structure, whose separations are proportional to twice the length of the DS⁻ group (ca. 3.5 nm based on XRD and molecular modeling)^{45,46} plus twice the ionic radius of the corresponding metal ion $(r_{\rm M}^{n+})$ (Table 1).⁴⁷ This trend was observed for all the trivalent metal dodecyl sulfates, including the reflections of $Al(DS)_3$ at lowest q, supporting the idea of a lamellar structure. Lee and coworkers¹⁸ have suggested from the interlamellar spacings that with $Gd(DS)_3$ prepared at pH < 7 that there is tilting of the lamellar bilayer relative to the metal plane. Our results are consistent with this idea. However, as we will see later, there is evidence for slight conformational disordering in the alkyl chains, which will also reduce interlamellar spacings.

We believe that the metal ions are present in a twodimensional (2D) plane with a relatively homogeneous distribution, and are coordinated by sulfate (and in some cases water). Support for this comes from a recent study of closely related lanthanide surfactant lamellar assemblies,¹¹ where transmission electron microscopy (TEM) and SEM-EDS measurements showed the trivalent metal ions are present in an organized 2D structure. This is also consistent with results of Langmuir-Blodgett films formed from trivalent lanthanide ions and surfactants.48 Based on this and the structural parameters involved in the lamellar spacings of this type of material,⁴⁹ there should be a linear relationship between these spacing and the ionic radii. However, from a plot of the d_1 spacing as a function of $r_{\rm M}^{n+}$ (Fig. 3) the monovalent Na⁺ ion shows a larger interlamellar spacing than expected from its ionic radius. Although it may be thought that this is due to

hydration of the cation, as we will show below, this explanation can be ruled out from TGA data, which shows the smallest number of bound water molecules for the Na⁺based complex. Instead, we believe that in the $M(DS)_n$ systems there are significant differences in the conformational arrangement of the alkyl chains, essentially dictated by packing restrictions. As with other lipid systems,⁵⁰ in metal complexes of long chain amphiphiles the alkyl chains are normally thought to be fully extended and to adopt all-trans conformations.⁵¹ However, single crystal XRD studies on copper(II) decanoate⁵² show that, while one of the chains has this all-trans conformation, the other is distorted by rotation of bonds connecting the methylene groups closest to the anionic head group to ensure maximum packing. We suggest that a similar conformational disordering occurs to M(DS)₃ systems, but not with SDS, explaining why the sodium complex does not behave as the other compounds (Fig. 3). XRD and molecular modelling studies on anhydrous sodium dodecyl sulfate suggest a fully extended alkyl chain.⁴⁶ The observed decrease in the lamellar bilayer thickness of SDS on increasing hydration is suggested to result from increased chain tilting. The shifts in the signals of the terminal methylene peaks noted in the ¹H and ¹³C NMR spectra of the trivalent dodecyl sulfates give support to the idea of conformational disordering. Although, caution needs to be exercised with this argument, since the NMR spectra are observed in solution where aggregation effects may be important,⁵³ literature data on ²H NMR spectra of a heterogeneous system containing sodium dodecyl sulfate adsorbed at the alumina/water interface show conformational disordering of the α -methylene group.54

Interestingly, while the La(DS)3, Gd(DS)3 and SDS complexes produce a single lamellar structure (Fig. 2(b) and Table 1), in the case of $Al(DS)_3$ and $Cr(DS)_3$, the main lamellar phase coexists with two other lamellar structures (Fig. 2(a), Fig. S1[†] and Table 1), indicating the presence of extra ordering. A common structure with interlamellar spacing less ($d_3 = 2.649$ nm, dotted blue vertical lines in Fig. S1[†]) than those of the main lamellar phases of $Al(DS)_3$ ($d_1 = 3.029$ nm, continuous blue vertical lines in Fig. S1[†]) and $Cr(DS)_3$ ($d_1 = 3.056$ nm, continuous green vertical lines in Fig. S1[†]) is detected. A superstructure with higher interlamellar spacing ($d_2 = 3.273$ nm, dotted green vertical lines in Fig. S1[†]) also emerges concomitantly in both compounds. Previous reports^{55,56} have attributed the formation of extra ordering in structurally analogous systems to the entrapment of water molecules. We will return to this particular issue shortly. Finally, it is worth mentioning that the XRD patterns of Al(DS)₃ and Cr(DS)₃ provide evidence that the three lamellar structures referred above coexist with the lamellar order of the SDS phase.

The SEM images reproduced in Fig. 4 show the morphology of three representative samples of the metal dodecyl sulfate complexes: $Al(DS)_3$, $Cr(DS)_3$ and $La(DS)_3$. These compounds were produced as dense aggregates (Fig. 4(a), 4(e) and 4(k), respectively) which, in the case of the La³⁺-based compound, are homogeneously dispersed (Fig. 4(i) and 4(j)). The aggre-



Fig. 4 SEM images of the Al(DS)₃ (a)-(d), Cr(DS)₃ (e)-(h) and La(DS)₃ (i)-(l) complexes.

gates share in common a rather irregular shape, but differ considerably in terms of size (average diameters of *ca.* 200–100 μ m for Al(DS)₃ (Fig. 4(a)) and Cr(DS)₃ (Fig. 4(e)) and *ca.* 10 μ m for La(DS)₃ (Fig. 4(k)). Higher magnification shows that in the Al(DS)₃ and Cr(DS)₃ samples these micro-objects are composed of randomly organized microplatelets assembled along an edge-to-face fashion, giving rise to an "origami"-like morphology (Fig. 4(b) and 4(f), respectively). In the case of Cr(DS)₃, the surface of the micro-objects exhibits a waxy appearance (Fig. 4(g)). The right bottom area of Fig. 4(l) reveals that in the case of La(DS)₃ these platelets are made of lamellae of nanometer thickness. In La(DS)₃ thin films with submicrometer thickness stack along a sort of tile-to-tile piling (Fig. 4(l)).

On the basis of elemental analysis performed on microscopic sections of $Al(DS)_3$, $Cr(DS)_3$, $La(DS)_3$ and $Gd(DS)_3$ by EDS (Fig. S2†) the atomic percentage of Al, Cr, La and Gd, and of S was calculated to be 22.40 and 77.60%, 21.35 and 78.65%, 26.02 and 73.98%, and 16.17 and 83.83%, respectively, suggesting the 1 : 3 stoichiometry. X-ray mapping of a zoom area of Fig. 5(a), 5(d) ,5(g) and 5(j) demonstrated that in these samples, as expected, the S atoms are found all over the surface of the aggregates (Fig. 5(b), 5(e) , 5(h) and 5(k), respectively). Fig. 5(c), 5(f) , 5(i) and 5(l) demonstrate that the Al^{3+} , Cr^{3+} , La^{3+} and Gd^{3+} ions are also homogeneously distributed, respectively. These results show that the metalsurfactant ratio at the surface is identical to that in the bulk material. This may be relevant to the superstructuring which we will discuss later.

The texture of $La(DS)_3$, which yields a single lamellar structure (see above), was further analyzed by AFM upon scanning the surface of this complex in tapping mode (Fig. 6). The 3D perspective of the complex, depicted in Fig. 6(a), confirms its lamellar arrangement. The average periodicity observed in the amplified 2D image (Fig. 6(b)) is approximately

4 nm, according to the profile plot of Fig. 6(c). It is quite interesting that the lamellar structuring observed with the XRD (*ca.* 3.647 nm, Table 1) and AFM (*ca.* 4 nm) studies coincides beautifully.

The thermal behaviour of metal dodecyl sulfate compounds is expected to depend upon the presence of water, the



Fig. 5 SEM images of the Al(DS)₃ (a) (zoom of Fig. 4(a)), $Cr(DS)_3$ (d) (zoom of Fig. 4(e)), $La(DS)_3$ (g) (zoom of Fig. 4(j)) and $Gd(DS)_3$ (j) complexes and corresponding EDS mapping for S ((b), (e), (h) and (k), respectively) and La ((c), (f), (i) and (l), respectively).



Fig. 6 AFM Phase images of the $La(DS)_3$ complex: 3D (a), 2D (b) and profile plot (c) corresponding to the line drawn in (b). The vertical lines are guides for the eyes.

stereochemistry of the metal ion and the associated anions, and the experimental conditions.⁵⁷ TGA and DSC measurements were used to study the thermal behaviour of the $M(DS)_3$ complexes examined in the present work. The results for Gd(DS)₃ are very similar to those reported by Lee *et al.* for their sample prepared at pH 6.¹⁸

The TGA curves for all the samples over the 25-900 °C range (Fig. 7) show different trends of weight loss which can been divided into three main temperature ranges, designated as regions I, II and III. Region I is reproduced in detail in Fig. 8; Regions II and III are represented in Fig. S3(a) and S3(b),† respectively.

The analysis of Region I, which corresponds to the first step of weight loss taking place from room temperature to 140 $^\circ C$,

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Fig. 7 TGA curves of the metal dodecyl sulfate complexes M(DS)_n.

is extremely valuable, as it provides information regarding the release of water molecules and the formation of the anhydrous complexes.⁵⁸ Although all the samples undergo a mass loss within this temperature interval, Fig. 8 and Table 2 provide evidence that there is a trend in the compounds for the water content to increase in the order: $SDS < La(DS)_3 < Gd(DS)_3 <$ $Cr(DS)_3 < Al(DS)_3$. Clearly, $Al(DS)_3$ and $Cr(DS)_3$ are the compounds which display the most complex TGA curves (Fig. 8). In both cases the process of water loss begins already at 40 °C and ends up at about 112 °C (Table 2). These results strongly suggest not only the existence of both occluded and bound water molecules, but also the occurrence of a large amount of water in these two compounds. Based on the weight variation corresponding to the water loss measured over this temperature range (Table 2), it was possible to estimate the number of water molecules (x) present in the $M(DS)_n \cdot xH_2O$ complexes: x = 0.1, 4.1, 3.2, 0.7 and 2.0 for M = Na⁺, Al³⁺, Cr³⁺, La³⁺ and Gd³⁺, respectively. The number of water molecules



Fig. 8 TGA curves (left axis) of the metal dodecyl sulfate complexes $M(DS)_n$ in the 20–140 °C temperature range (region I of Fig. 7) and corresponding derivative curves (right axis).

Table 2 Relevant TGA data of the metal dodecyl sulfate complexes

Region		SDS	Al(DS) ₃	$Cr(DS)_3$	$La(DS)_3$	Gd(DS) ₃
I	$T/^{\circ}\mathbf{C}$		40	40	99	40
			63			
			72	72		72
			84	90		
		98				100
			112	112		
	Weight loss (%)	0.8	8.3	6.3	1.3	3.7
II	T/°C	220	148		182	162
		253	164	156	206	186
	Weight loss (%)	72.7	53.0	76.5	57.2	70.0
III	T/°C				358	338
				422		
			465	482		
			541		521	521
					588	560
					648	626
		720				
	Weight loss (%)	5.9	13.4	10.9	17.3	21.0

determined for La(DS)₃ and Gd(DS)₃ are in perfect agreement with those previously reported for other lanthanide surfactant complexes.⁵⁹ On the basis of these findings, the formulae of the compounds are SDS·0.1H₂O, Al(DS)₃·4.1H₂O, Cr(DS)₃·3.2H₂O, La(DS)₃·0.7H₂O and Gd(DS)₃·2.0H₂O.

In an attempt to deduce the thickness of the water layer between two consecutive bilayers d_W (Fig. 3 and 9, and Table 1), the dilution law employed by Pacios *et al.* for the lamellar liquid crystal formed by the surfactant sodium bis-2ethylhexyl sulfosuccinate (AOT) in water⁶⁰ was adopted:

$$1/d = (1/d_0)\varphi_{\rm S} \tag{1}$$

$$d = d_0 + d_W \tag{2}$$

where *d* is the repeat distance between lamellae and d_0 is the thickness of the AOT bilayer. In the present case d_0 corresponded to the spacing d_1 and φ_S represented the molar fraction of the metal dodecyl sulfate complex in the (metal dodecyl sulfate complex+water) mixture instead of the volume fraction of the surfactant in the (surfactant+water) mixture in the original equation. Fig. 3 shows that the variation of the thickness of the interlamellar water layer d_W with the ionic radii follows a linear relationship in the case of the complexes incorporating a trivalent metal ion. The formation of superstructures in the case of the Cr^{3+} and Al^{3+} -based compounds is understandable considering the magnitude of d_W (see a schematic representation in the Fig. 9).

The dehydration and other thermal processes of all the metal dodecyl sulfate complexes were also followed by means of DSC measurements. An endothermic peak correlated with water loss was detected in the DSC curves of $Al(DS)_3$ (broad and highly structured), $Cr(DS)_3$ (broad and sharp), $La(DS)_3$ (sharp and intense), $Gd(DS)_3$ (structured) and SDS (sharp with shoulder) (Fig. 10). On second heating, this peak was absent, in agreement with its attribution to dehydration. In the case of the Al^{3+} -based complex it was not possible to deduce the



Fig. 9 Schematic view of the characteristic distances of the lamellar bilayer of the metal dodecyl sulfate complexes $M(DS)_{n}$.

dehydration onset temperature (T_{onset}) because of the complex endotherm profile. For the other four complexes, T_{onset} values of approximately 71, 99, 111 and 98 °C, respectively, were determined (Table 3). The good agreement between these values and those obtained from TGA data (Fig. 8 and Table 2), *i.e.*, 72, 99, 100 and 98 °C, is satisfying. Other observable endothermic peaks discerned in the DSC curves of Fig. 10 correspond to formation of typical intermediate liquid crystalline^{49,53} or other⁶¹ mesophases. We also note that the melting



Fig. 10 DSC curves of the metal dodecyl sulfate complexes M(DS)_n.

 Table 3 Relevant DSC and PLTM data of the metal dodecyl sulfate complexes.

 vS - very strong, S - strong, m - medium, w - weak, vw - very weak, sh - shoulder

$M(DS)_n$		DSC	DI TM		
<i>n</i> = 1	<i>n</i> = 3	$T_{\mathrm{peak}} (^{\circ}\mathrm{C})$	$T_{\text{onset}} (^{\circ}\mathrm{C})$	T_{onset} (°C	
Na ⁺		18 (m) 100(m)	98	а	
	Al^{3+}	108 (sh) 28 (vw) 49 (vw)	b	67	
		59(sh) 64(S)			
	Cr ³⁺	71(S) 28 (vw) 70 (S)	71	75	
	La ³⁺	79 (vw) 115 (vS)	99	96	
	Gd ³⁺	108 (m) 115 (m) 130 (sh)	111	104	
^{<i>a</i>} Not an	alyzed. ^b Not	calculated.			

temperatures of the complexes occur at temperatures greater than 140 $^\circ \rm C.$

The thermal behaviour of the samples below 140 °C was further evaluated by PLTM. Fig. 11 shows that Al(DS)₃ and $Cr(DS)_3$ dehydrate at lower temperatures than $La(DS)_3$ and $Gd(DS)_3$, in agreement with the TGA and DSC results. The images obtained by PLTM allow us to easily follow the dehydration process in Al(DS)₃ and Cr(DS)₃ by the appearance of rounded boundaries (Fig. 12(a) and 12(b) and Fig. 12(c) and 12(d), respectively). In contrast, the changes in the PLTM images of La(DS)₃ and Gd(DS)₃ are very subtle (Fig. 12(e) and 12(f) and Fig. 12(g) and 12(h), respectively), although they are very well detected using light intensity signal measurement (Fig. 11(b)), a particularly useful technique in these cases. Another clear advantage of the PLTM measurements lies in the fact that the calculation of the T_{onset} for dehydration is considerably easier than with DSC. It was possible to deduce the T_{onset} value for Al(DS)₃ (67 °C) (Table 3), which was unreliable in the DSC measurements.

The decomposition of the anhydrous complexes takes place above 140 °C. This occurs in the temperature ranges corresponding to Regions II (140 $< T \le 300$ °C) and III (300 $< T \le 900$ °C) (Fig. 7). A sharp mass loss is evident in Region II (Fig. S3(a)[†] and Table 2). The degradation process that occurs here is likely to be associated either with cleavage of the bond between the alkyl chains and the sulfate group or the sulfate ester bond.⁵⁸

The decomposition for $Cr(DS)_3$ takes place abruptly in a single step, with a mass loss maximum at 156 °C (Fig. S3(a)†). In contrast, with all the other metal dodecyl sulfates, the decomposition in Region II involves two-step processes (Fig. S3(a)†). The temperatures of maximum mass loss depend on the nature of the compound, and is lowest for Al(DS)₃ and highest for La(DS)₃ among the trivalent metal salts, while SDS



Fig. 11 PLTM curves of the trivalent metal dodecyl sulfate complexes $M(DS)_3$ accompanied by (a) DSC signal and (b) light intensity signal.

has the highest maximum mass loss temperature for all the compounds studied (Table 2). Interestingly, the global trend observed for the degradation Tonset of the anhydrous complexes $(Al(DS)_3 < Cr(DS)_3 < Gd(DS)_3 < La(DS)_3 < SDS)$ is exactly the inverse order found for the water release T_{onset} from the aquocomplexes. The fact that the temperatures corresponding to the cleavage of the alkyl chains of trivalent metalbased complexes $M(DS)_3$ complexes are lower than the temperature with the monovalent salt SDS is in agreement with previous reports for cerium tri(dodecyl sulfate),⁶ for a MCM-41-type material,⁶² and for SDS strongly bound to the surface of mesoporous alumina.⁶³ This suggests that there is a stronger interaction between the surfactant headgroup and the metal ions in the $M(DS)_3$ compounds than in SDS. We will return to this particular aspect below, in the section devoted to the FT-IR analysis of the local environment of the sulfate headgroup. Whilst no attempts were made at product identification, based on reports on basic lead(II) dodecylsulfate, the degradation of the metal dodecyl sulfate complexes in Region II is likely to lead to the formation of dodecanol⁶⁴ and the metal sulfates, $M_2(SO_4)_3$. This latter assertion was confirmed by FT-IR spectroscopy, where the spectra of the



Fig. 12 PLTM images of $Al(DS)_3$ (30 °C (a) and 70 °C (b)), $Cr(DS)_3$ (30 °C (c) and 80 °C (d)), $La(DS)_3$ (30 °C (e) and 120 °C (f)) and $Gd(DS)_3$ (30 °C (g) and 120 °C (h)).

 $M(DS)_3$ complexes after treatment at 900 $^\circ C$ (data not shown) only exhibited a characteristic band ascribed to the sulfate group.

Following carbon chain cleavage, the final degradation of all the metal dodecyl sulfate complexes occurs in Region III (Fig. 7). At the highest temperature studied, the Cr^{3+} and Gd^{3+} -based complexes are fully decomposed to form the metal sulfates. However, with the other compounds studied, a considerable amount of residue still remains (20–26% of the sample mass) at the same temperature (Fig. 7). The series of peaks detected in the TGA derivative curves of Fig. S3(b)[†] above 550 °C might be linked to the combustion of residual organic matter. Above 700 °C no signals are observed in the TGA derivative curves (Fig. S3(b)[†]).

The FT-IR spectra obtained for the samples in the present study (Fig. S4 and S5^{\dagger}) are similar to those reported for related materials.^{6,44,49,65-67}

Rich information on the degree of chain packing and the *trans/gauche* conformational ratio in alkyl chains of the solid metal dodecyl sulfate complexes can been retrieved from the FT-IR spectra. Three diagnostic modes of the alkyl chains were

analyzed: the symmetric and asymmetric stretching CH₂ modes (v_s CH₂ and v_a CH₂, respectively) and the CH₂ bending (δ CH₂) mode.

The frequency, width and height of the FT-IR v_s CH₂ and v_a CH₂ bands are sensitive to the *gauche/trans* conformer ratio and to intermolecular interactions between the alkyl chains.

While the position and intensity of the v_s CH₂ mode depend on Fermi resonance between the v_s CH₂ fundamental with the overtones of the δ CH₂ vibrations, the v_a CH₂ mode is sensitive to coupling of the chain torsional and rotational motions.^{68–72} The FT-IR v_s CH₂ and v_a CH₂ bands of all-*trans* conformers of alkylchains are expected in the 2846-2849 and 2919 cm⁻¹ ranges, respectively.^{70–76} In the case of alkyl chains adopting *gauche* conformations, the FT-IR v_s CH₂ and v_a CH₂ bands are upshifted and emerge at 2856–2858 and 2924–2928 cm⁻¹, respectively.^{75,76}

The FT-IR spectra of all the metal dodecyl sulfate complexes except $Cr(DS)_3$ are dominated by two bands at 2918 cm⁻¹ (very strong, vS) and 2850 cm^{-1} (strong, S) (Fig. S4(b)[†] and Table 4), assigned to the v_aCH_2 and v_sCH_2 modes, respectively, indicating that a considerable fraction of the alkyl chains are fully stretched (all-trans) and densely packed. However, the shoulder which emerges at about 2928 cm⁻¹ in the spectra of all the complexes (Fig. S4(b)[†] and Table 4) demonstrates that gauche and all-trans conformers coexist in these compounds. The band profiles in the FT-IR spectra of $Cr(DS)_3$ are significantly different: the v_aCH₂ and v_sCH₂ bands are markedly broader and their intensity maxima are shifted to higher wavenumbers (2922 and 2854 cm⁻¹, respectively) (Fig. S4(b)[†] and Table 4). These findings prove that the proportion of partially disordered alkyl chains is much higher in the Cr³⁺based complex than in the other four complexes studied.

Similar conclusions may be drawn from inspection of the signature of the metal dodecyl sulfate complexes in the δCH_2 region of the FT-IR spectra. The analysis of this band is particularly useful, because its position, intensity and band shape are sensitive to interchain interactions and chain packing.^{76,77} A higher frequency ($\sim 1472 \text{ cm}^{-1}$) indicates the presence of ordered alkyl chains along extended, all-trans zigzag, conformations. In contrast, lower frequencies (~1466 cm⁻¹), broadening and weakening of the intensity provide evidence of a larger gauche/trans conformer ratio and consequently the occurrence of larger population of disordered alkyl chains.^{76,77} The FT-IR spectra in the δCH_2 region of all the metal dodecyl sulfate complexes display a prominent band centered at about 1468 cm^{-1} and a shoulder at 1478 cm^{-1} (Fig. S4(c)[†] and Table 4), thus confirming that the alkyl chains of all these compounds contain simultaneously all-trans and gauche conformers. It has been reported that the presence of gauche bonds is accompanied by the development of a band at ca. 1440 cm^{-178,79} which is not the case here (Fig. S4(c)[†]). While the FT-IR data indicate some conformational disordering of the alkyl chains in these metal dodecyl sulfates, they do not indicate either the extent or location. However, further information can be obtained from molecular dynamics simulations on n-alkanes,80 which have demonstrated the

Table 4 Frequency (in cm ⁻¹) and assignment of	characteristic bands of the FT-IR the me	etal dodecyl sulfate comp	blexes M(DS) _n ^{68–77,81–86,89–95}
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n = 1 Na ⁺	<i>n</i> = 3				Assignment ^a	Conformations	
	Al ³⁺	Cr ³⁺	La ³⁺	Gd ³⁺			
2928 sh	2928 sh	2922 sh		2928 sh	$v_{a}(CH_{2})$	gauche	
2918	2918		2918	2919		all-trans	
		2854			$v_{s}(CH_{2})$	gauche	
2850	2851		2851	2851		all-trans	
1478 sh	1478 sh	1478 sh	1478 sh	1478 sh		all-trans	
1468	1469	1468	1468	1468		gauche	
1458 sh	1459 sh	1458	1458 sh	1458 sh		not assigned	
1271 sh	1272 S	1272 sh	1273 sh	1273 sh	$v_{a}(SO_{4})$ coordinated		
1257 vS	1257 sh	1259 sh	1257 sh	1257 sh			
1237 sh	1237 sh	1237 sh	1237 vS	1237 vS			
1225 vS	1211 vS	1213 vS	1222 vS	1215 vS			
1185 vS	1189 vS	1186 sh	1184 S	1193 vS	M-O(····H)SO ₂ ^{$n-1$}		
1172 sh	1172 sh	1173 sh	1172 sh	1173 vS	- () 3		
1157 sh	1157 S	1163 sh	1163 sh	1157 S			
1090 S				1090 S	$v_{-}(SO_{4})$ coordinated		
1077 m	1077 m	1077 sh	1077 sh	1077 sh	(sold) coordinated		
1077 111	1077 111	1063 S	1065 S	1077 511			
1045 m	1045 m	1045 sh	1044 m	1044 m	$M = \Omega(\dots H) S \Omega_n^{n-1}$		
801 w	801 viv	1010 511	1011 111	801 viv	M 0(11)003		
091 W	091 VW			051 VW			
832 sh					$v_{\rm s}({ m C-OSO_3})$		
^{<i>a</i>} vS – very stre	ong; S – strong; m –	medium; w – weak; s	sh – shoulder.				
^{<i>a</i>} vS – very stre	ong; S – strong; m –	medium; w – weak; s	sh – shoulder.				

various types of defects possible. To be consistent with the XRD long spacings, it is not possible to have random disordering along the alkyl chains, otherwise the reflections would not be sharp. Instead, it is probable that relatively localized disordering occurs close to the terminal sulfate group. This suggests end-*gauche*, kink or jog structures.⁸⁰ The NMR results presented earlier are fully consistent with this view.

Although it would be valuable to carry out detailed analysis of the $3700-3000 \text{ cm}^{-1}$ interval of the FT-IR spectra of SDS, $Al(DS)_3$, $Cr(DS)_3$, $La(DS)_3$ and $Gd(DS)_3$, where the characteristic OH stretching modes of water absorb, this is complicated by bands from adsorbed water from the potassium bromide pellets used, and the results for all the systems given in Fig. S4(a)† should only be considered for reference purposes.

The FT-IR spectral signature of the SDS, Al(DS)₃, Cr(DS)₃, La(DS)₃ and Gd(DS)₃ complexes in the region where the main absorption bands of the RSO₄⁻⁻ ion are expected (1350–750 cm⁻¹ interval) is shown in Fig. S5†. A general discussion of the vibrations of the sulfate group is given in the ESI.† The analysis of these spectra is complicated by the fact that some of the most characteristic sulfate modes are superimposed with the skeletal C–C stretching (vC–C) vibration modes of the alkyl chains (Table 4). The attribution of the RSO₄⁻⁻ bands of the metal dodecyl sulfates (Table 4) will essentially rely on published infrared spectroscopic studies dealing with SDS, a Pr-based surfactant mesophase templated by the dodecyl sulfate ion (DS⁻),^{81–83} gadolinium dodecyl sulfate¹⁸ and on a

series of alkali palmityl (hexadecyl) sulfates,⁸⁴ which may be considered as close analogs of the metal dodecyl sulfate complexes.

Globally, the profile of the FT-IR spectrum of $Al(DS)_3$ closely resembles that of $Gd(DS)_3$, while strong similarities are also observed between the $Cr(DS)_3/La(DS)_3$ pair (Fig. S5†). The most noteworthy aspect of the FT-IR spectrum of SDS is that the lowfrequency side of the v_aSO_4 band differs considerably from those of the trivalent metal dodecyl complexes (Fig. S5†).

The strong feature that emerges at 1107 cm^{-1} in the spectra of SDS·0.1H₂O is assigned to the v_a SO₄ mode, indicating the presence of "free" anions.^{85,86} This event is also detected in the spectra of the trivalent metal-based analogues (Table 4), and is consistent with the XRD results discussed earlier.

The strong chemical resemblance between SDS and sodium palmityl sulfate⁷⁶ allowed us to associate the shoulder at 1271 cm⁻¹, the very strong events at 1257, 1237 and 1225 cm⁻¹ and the intense event at 1090 cm⁻¹ to the v_aSO_4 mode and the strong band at 1090 cm⁻¹ and the medium intensity band at 1077 cm⁻¹ to the v_sSO_4 mode of the anion coordinated with Na⁺ (Table 4). The various v_aSO_4 components correspond to different directions of the transition dipole moment.⁸² Comparison of these results with those of the trivalent metal docecyl sulfates (Table 4) suggests that the v_aSO_4 mode is correlated with the nature of the cation, unlike in the case of metal palmityl sulfates.⁸⁴ The shift of the strong SDS v_aSO_4 component at 1225 cm⁻¹ to lower wavenumbers for the trivalent metal dodecyl complexes indicates that the dodecyl sulfate is complexed by the metal. This is similar to what is observed in metal complexes of sulfonic acid salts (R– SO₃⁻:M⁺),⁸⁷ and suggests strong, essentially electrostatic, interactions between trivalent metal ions and dodecyl sulfate. In the v_sSO_4 region the 1090 cm⁻¹ feature undergoes a shift to 1063 and 1065 cm⁻¹ in the case of Cr(DS)₃ and La(DS)₃, respectively (Fig. S5† and Table 4). This downshift may be interpreted as an indication, not only that the *M*–O bond is about the same order of magnitude in both compounds, but also that the *M*–O bond is stronger in these two complexes than in SDS, Al(DS)₃ and Gd(DS)₃.

The presence of hydrogen bonding interactions between the water molecules belonging to the first coordination sphere of the metal ions and the sulfate ions along a monodentate fashion (C_{3v}) is highly likely. Based on the assignment proposed by Hug for the $[Fe(III)(H_2O)_5SO_4]^+$ complexes formed in hematite,⁸⁵ the prominent band at 1185 cm⁻¹, the shoulder at 1172 cm⁻¹, the medium intensity event located at 1045 cm⁻¹ and the weak feature detected at 891 cm⁻¹ detected in the spectrum of SDS·0.1H₂O (Fig. S5†) are associated with the occurrence of M-O(…H)SO₃ⁿ ⁻¹ species (Table 4). The shoulder observed at 1157 cm⁻¹ (Fig. S5†) is tentatively ascribed to a similar charged species in which the strength of the *M*-O bond is different.

Based on XRD and FT-IR analyses, the structure of $M(DS)_3$ is suggested to be packed in a head-to-head, tail-to-tail bilayered arrangement with the alkyl chains tilted from the (001) plane, and an interlayer distance of $d_{001} = 3.04$, 3.06, 3.63 and 3.53 nm, for Al(DS)₃, Cr(DS)₃, La(DS)₃ and Gd(DS)₃, respectively. This kind of complexes organization is common on metal surfactant mixtures.^{59,88}

The FT-IR patterns of $M(DS)_3$ did not match any of the hydrate forms of SDS,⁸⁵ but a similar splitting of the OSO₃ asymmetric stretching was reported for ammonium hexadecyl sulfate (NH₄HS).⁸⁴ However, the IR spectrum of NH₄HS also displays a splitting of the CH₂ bending and rocking modes, and an associated band at 1478 cm⁻¹ (α -CH₂ bending). This splitting pattern, characteristic of an orthorhombic subcell,^{82,84} was not observed in the M(DS)₃ spectra, which suggests that the high asymmetry of the OSO₃ group is actually caused by its interaction with M³⁺ cations. This is likely to affect local chain packing and supports the idea from the XRD data that there may be some conformational disordering of the methylene groups closest to the sulfate.

4. Conclusions

The dodecyl sulfates of the model trivalent ions of aluminium, chromium, lanthanum and gadolinium have been prepared by precipitation from aqueous solution at the natural pH and characterized by a variety of techniques. Layered lamellar structures are observed in all cases, with planes of metal ions, having varying degrees of hydration, separated by extended dodecyl sulfate chains. Differences are observed in coordination behavior between the metal dodecylsulfates, and there is good evidence for slight conformational disordering of the methylene groups close to the sulfate head group. The lamellar structuring evidenced by XRD was corroborated by AFM studies. Dehydration, followed at higher temperatures by alkyl chain cleavage, of the trivalent metal decylsulfates is observed upon heating. These results show a simple route under mild conditions for preparation of layered structures of trivalent metal ions of electronic, magnetic, optical and catalytic interest.

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