Supporting Information

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

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Fig. S1 XRD patterns of the metal dodecyl sulfate complexes M(SD)$_n$. 
Fig. S2 EDS spectrum of the Al(DS)$_3$ (a), Cr(DS)$_3$ (b), Gd(DS)$_3$ (c) and La(DS)$_3$ (d) complexes.
Fig. S3 TGA curves (left axis) of the metal dodecyl sulfate complexes M(DS)$_3$ and derivate curves (right axis) corresponding to Regions II (a) and III (b) of the plot of Fig. 7.
Fig. S4 FT-IR spectra of the metal dodecyl sulfate complexes M(DS)$_n$: in the νOH (a), ν$_s$CH$_2$ and ν$_a$CH$_2$ (b) and δCH$_2$ (c) regions.
**Fig. S5** FT-IR spectra of the metal dodecyl sulfate complexes M(DS)$_n$ in νC-C and sulfate regions.
Interpretation of FT-IR spectra for the sulfate group vibrations

Examination of the characteristic bands of the \( \text{SO}_4^{2-} \) ion in the FT-IR spectra of SDS.0.1H2O, Al(DS)3.4.1H2O, Cr(DS)3.3.2H2O, La(DS)3.0.7H2O and Gd(DS)3.2.0H2O is important to elucidate the interactions established by the dodecyl sulfate headgroup in each of these compounds. The attribution of the infrared spectrum of the sulfate ion is well established.\(^{82,\ 83}\) In aqueous solution, the “free” sulfate ion belongs to the tetrahedral \( T_d \) point group. For this symmetry only one broad vibration band, associated with the triply degenerate asymmetric stretching \( \nu_3 \) vibration mode (henceforth designated as \( \nu_\text{aSO}_4 \)), is infrared active, being located at approximately 1102 cm\(^{-1}\). In outer-sphere sulfate complexes, in which the \( \text{SO}_4^{2-} \) ion does not belong to the 1\(^{st}\) coordination sphere of the metal, distortion due to electrostatic effects may upshift the \( \nu_\text{aSO}_4 \) mode. In addition the \( \nu_1 \) band, ascribed to the non-degenerate symmetric stretching vibration mode and henceforth referred as \( \nu_\text{sSO}_4 \), may become infrared active, appearing as a weak band at about 980 cm\(^{-1}\). In the case of inner-sphere sulfate complexes, \( \text{i.e.} \), those in which the 1\(^{st}\) coordination shell of the metal comprises the \( \text{SO}_4^{2-} \) ligand, the symmetry of the anion is lowered and the degeneracy of the \( \nu_\text{aSO}_4 \) mode is lifted. In the case of monodentate bonding occurring via coordination to a metal (M-\( \text{OSO}_3 \)) or through protonation (H…\( \text{OSO}_3^{-} \) or simply HSO4\(^{-}\)) (\( C_3v \) symmetry) the \( \nu_\text{sSO}_4 \) band splits into two bands and the \( \nu_\text{sSO}_4 \) band emerges fully active at about 975 cm\(^{-1}\). If the \( \text{SO}_4^{2-} \) ion adopts bidentate configuration (binuclear (M-\( \text{O}_2 \)\( \text{SO}_2 \)) or bridging M-\( \text{O}_2 \text{SO}_2 \)), the symmetry is further lowered to \( C_{2v} \) and, as a consequence, the \( \nu_\text{sSO}_4 \) mode splits into three bands ranging between 1050 and 1250 cm\(^{-1}\), whereas the \( \nu_\text{sSO}_4 \) band is shifted to approximately 1000 cm\(^{-1}\).