

Supporting Information

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

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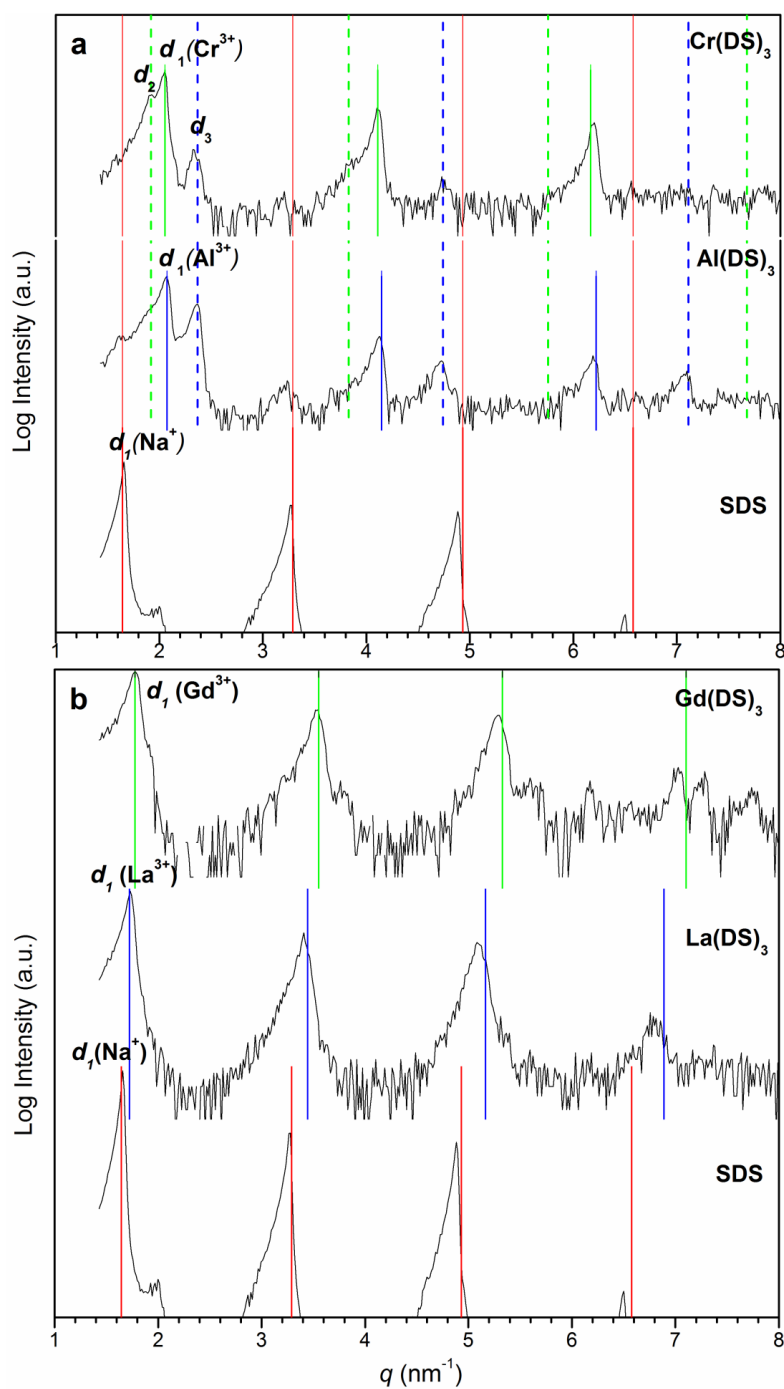


Fig. S1 XRD patterns of the metal dodecyl sulfate complexes $M(DS)_n$.

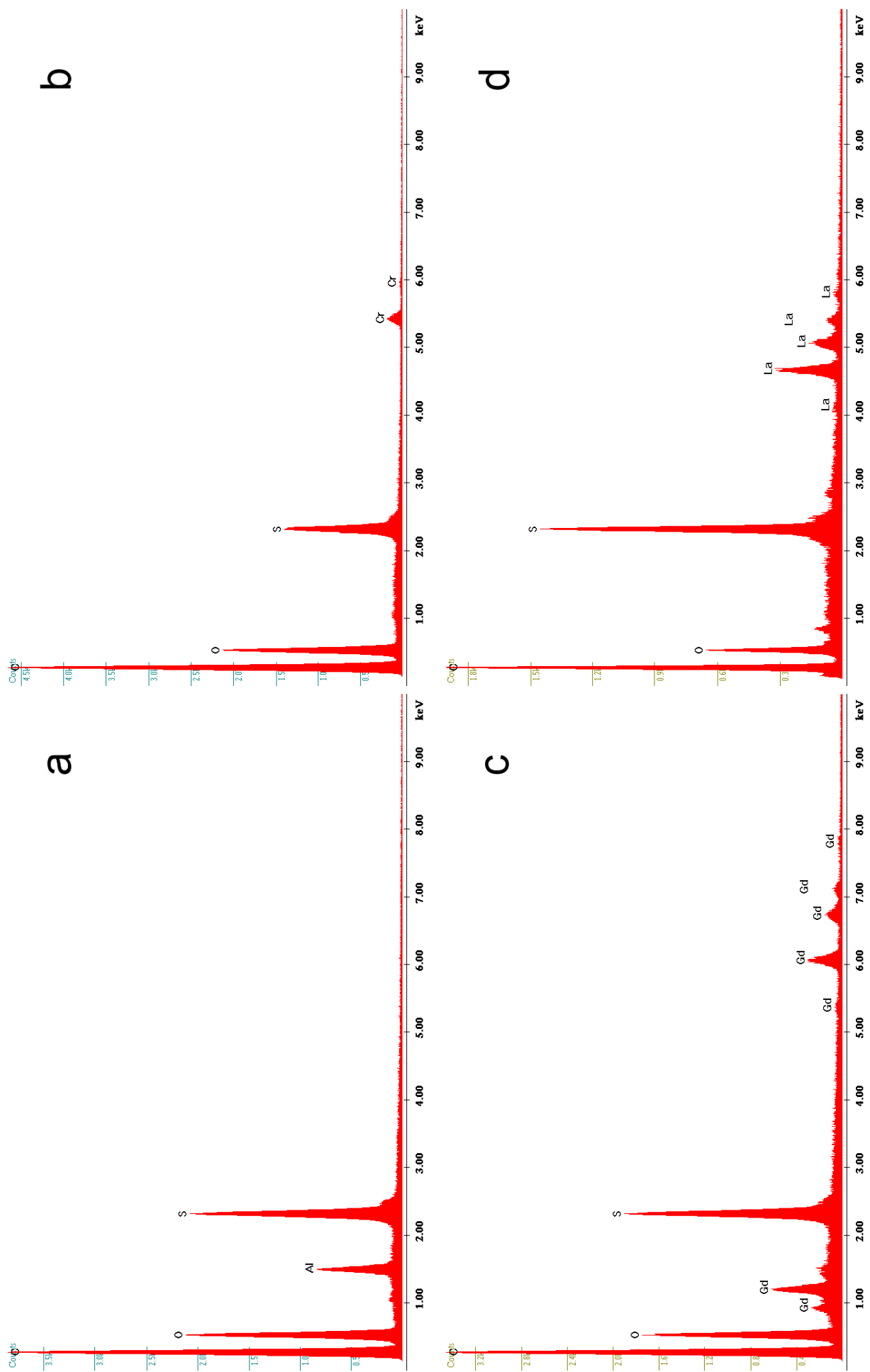


Fig. S2 EDS spectrum of the Al(DS)₃ (a), Cr(DS)₃ (b), Gd(DS)₃ (c) and La(DS)₃ (d) complexes.

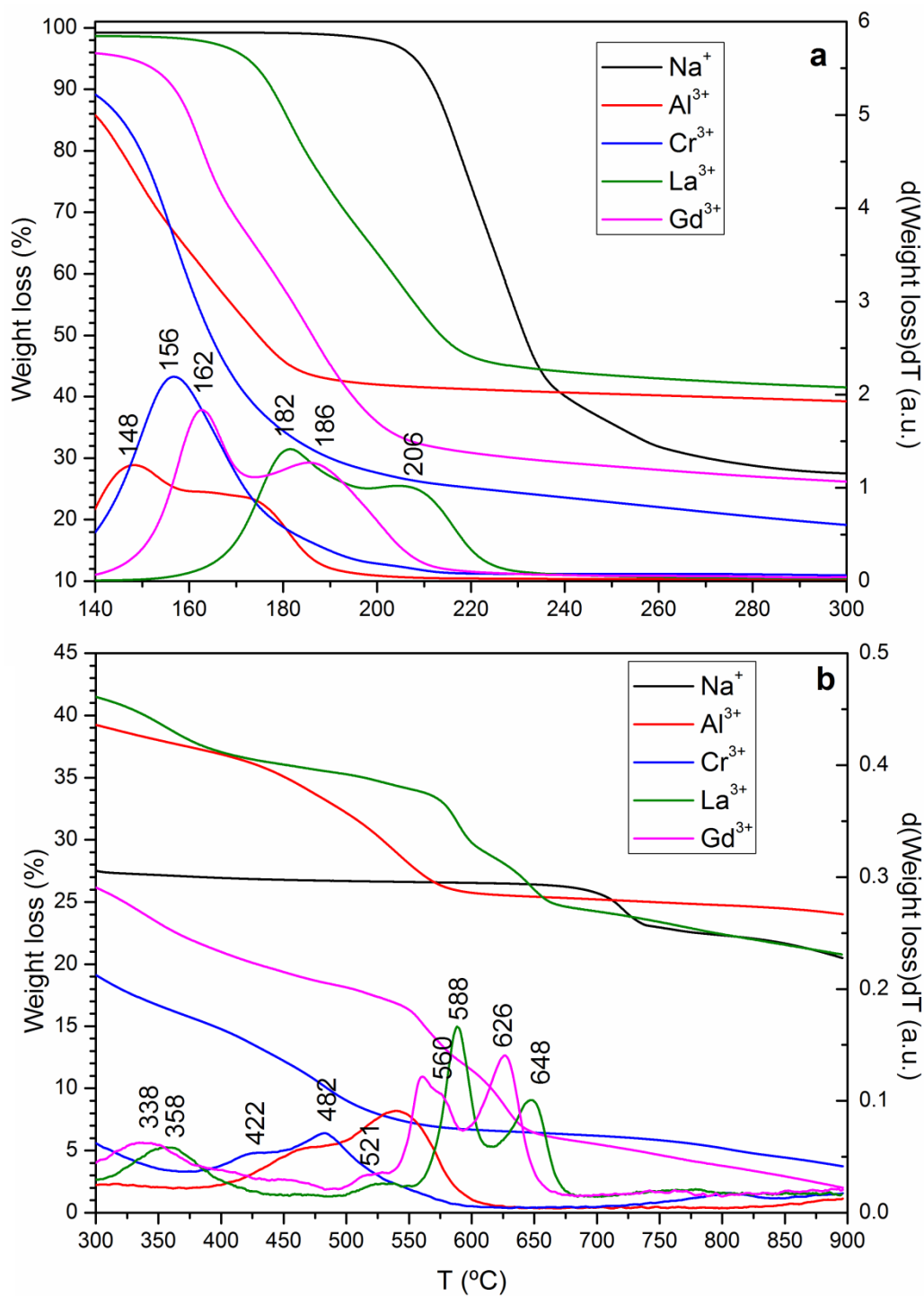


Fig. S3 TGA curves (left axis) of the metal dodecyl sulfate complexes $M(\text{DS})_3$ and derivative curves (right axis) corresponding to Regions II (a) and III (b) of the plot of Fig. 7.

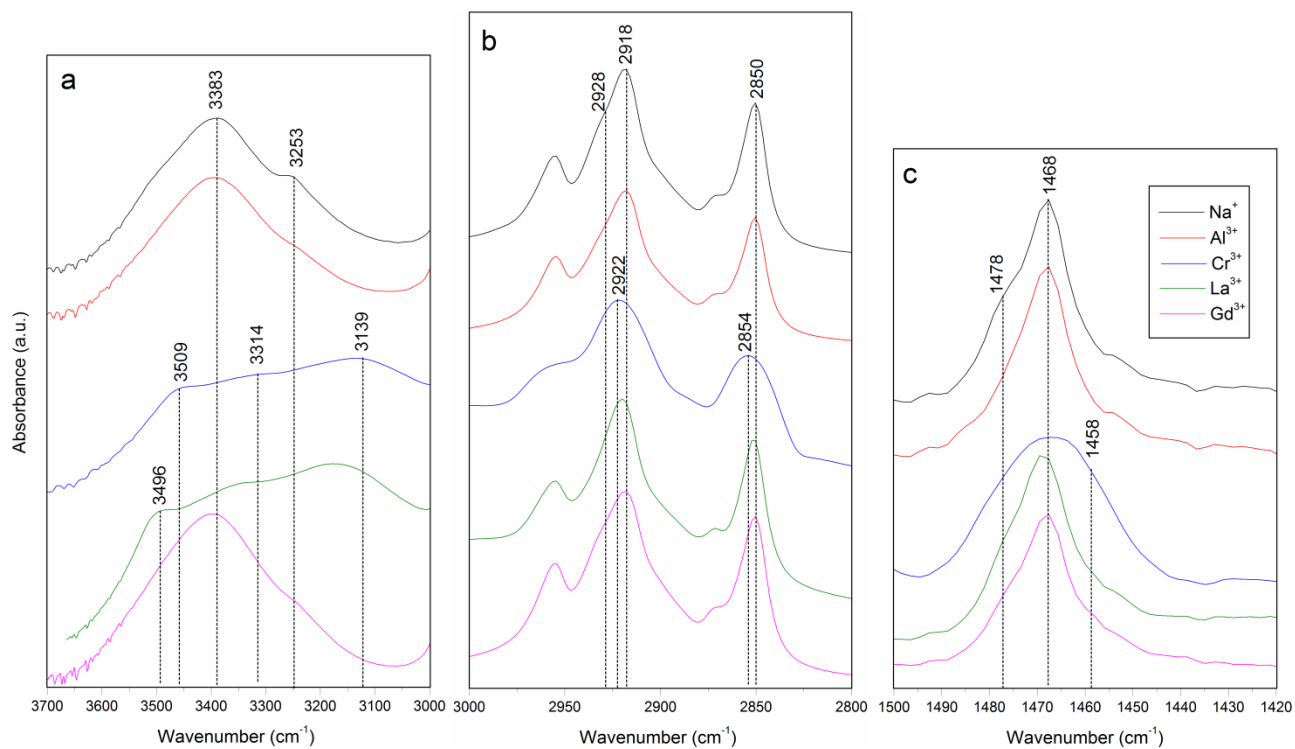


Fig. S4 FT-IR spectra of the metal dodecyl sulfate complexes $M(DS)_n$: in the νOH (a), $\nu_s CH_2$ and $\nu_a CH_2$ (b) and δCH_2 (c) regions.

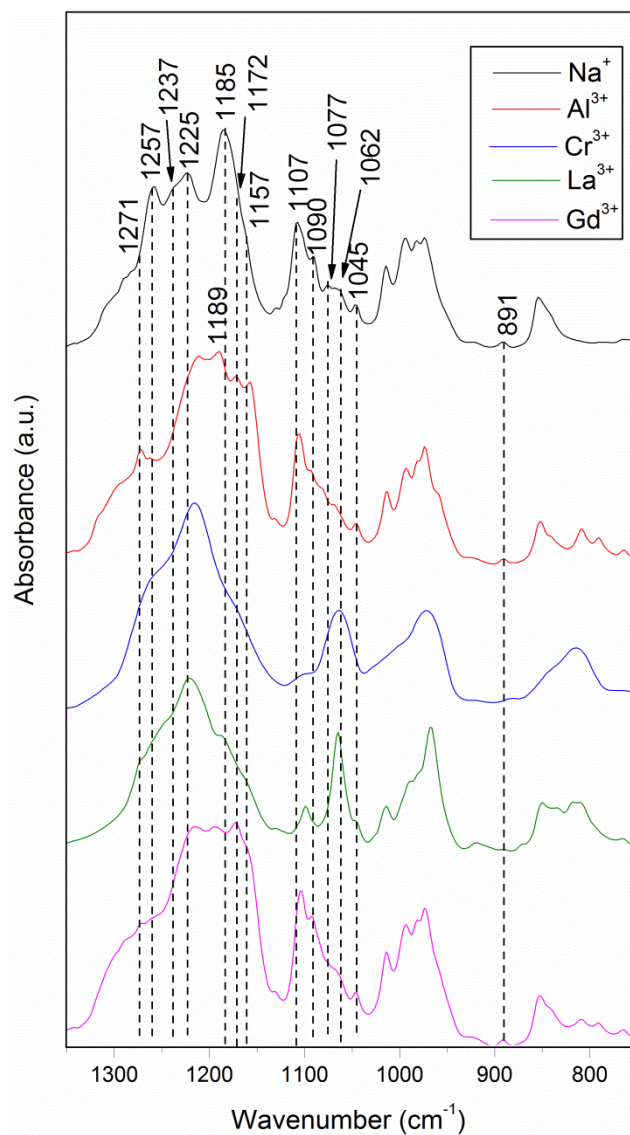


Fig. S5 FT-IR spectra of the metal dodecyl sulfate complexes $M(DS)_n$ in vC-C and sulfate regions.

Interpretation of FT-IR spectra for the sulfate group vibrations

Examination of the characteristic bands of the SO_4^{2-} ion in the FT-IR spectra of $\text{SDS}\cdot 0.1\text{H}_2\text{O}$, $\text{Al}(\text{DS})_3\cdot 4.1\text{H}_2\text{O}$, $\text{Cr}(\text{DS})_3\cdot 3.2\text{H}_2\text{O}$, $\text{La}(\text{DS})_3\cdot 0.7\text{H}_2\text{O}$ and $\text{Gd}(\text{DS})_3\cdot 2.0\text{H}_2\text{O}$ 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 ν_3 vibration mode (henceforth designated as $\nu_a\text{SO}_4$), is infrared active, being located at approximately 1102 cm^{-1} . In outer-sphere sulfate complexes, in which the SO_4^{2-} ion does not belong to the 1st coordination sphere of the metal, distortion due to electrostatic effects may upshift the $\nu_a\text{SO}_4$ mode. In addition the ν_1 band, ascribed to the non-degenerate symmetric stretching vibration mode and henceforth referred as $\nu_s\text{SO}_4$, may become infrared active, appearing as a weak band at about 980 cm^{-1} . In the case of inner-sphere sulfate complexes, *i.e.*, those in which the 1st coordination shell of the metal comprises the SO_4^{2-} ligand, the symmetry of the anion is lowered and the degeneracy of the $\nu_a\text{SO}_4$ mode is lifted. In the case of monodentate bonding occurring via coordination to a metal (M-OSO_3) or through protonation ($\text{H}\cdots\text{OSO}_3^-$ or simply HSO_4^-) (C_{3v} symmetry) the $\nu_a\text{SO}_4$ band splits into two bands and the $\nu_s\text{SO}_4$ band emerges fully active at about 975 cm^{-1} . If the SO_4^{2-} ion adopts bidentate configuration (binuclear $(\text{M-O})_2\text{SO}_2$ or bridging $\text{M-O}_2\text{SO}_2$), the symmetry is further lowered to C_{2v} and, as a consequence, the $\nu_a\text{SO}_4$ mode splits into three bands ranging between 1050 and 1250 cm^{-1} , whereas the $\nu_s\text{SO}_4$ band is shifted to approximately 1000 cm^{-1} .