Supporting Information

Experimental Section

General Synthesis Procedure

All reagents were purchased at high purity (AR grade) from AlfaAesar (croconic acid, C₅O₅H₂) and Strem Chemicals Sc(CH₃CO₂)₃·H₂O and were used without further purification.

The compound 1, with formula [Sc₇(croc)₆(OH)₇(H₂O)₆O]·4H₂O, can be prepared by hydrothermal reaction of 0.25 mmol of Sc(CH₃CO₂)₃·H₂O with 0.375 mmol of the ligand (C₅O₅H₂ = H₂croc) in a mixture of ethanol (5mL) and distilled water (3 mL). The mixture was heated in a Teflon-lined digestion bomb (internal volume of 43 mL), at 200 °C during 4-8 hours and then cooled rapidly to room temperature. Red dark rhombohedrical crystals suitable for the single crystal X-ray diffraction (XRD) study were collected after washing the obtained crystalline powder with distilled water and acetone (yield 57.50 %).

Crystal Structure Determination and Refinement

An appropriated single crystal of the compound 1 was mounted on a Bruker four circle kappa-diffractometer equipped with, a Cu INCOATEC microsource operated at 30W power (45kV, 0.60 mA) to generated Cu Kα radiation (λ = 1.54178 Å), and a Bruker AXIOM area detector (microgap technology). Diffraction data were collected exploring over a hemisphere of the reciprocal space in a combination of phi and omega scans to reach a resolution of 0.84 Å (58.91 ° in θ), using a Bruker APEX2 software suite (each exposure of 10s covered 0.5 ° in ω). Unit cell dimensions were determined by a least-squares fit of reflections with I >2 σ(I). Data were integrated and scaled using SAINTplus program¹.

Unit cell dimensions were determined by a least-squares fit of reflections with I >2 σ(I). A semi-empirical absorption and scale correction based on equivalent reflection was carried out using SADABS¹. Space group determinations were carried out using XPREP². The structure was solved by direct methods and refined by anisotropic full-matrix least-squares, except for hydrogen atoms as hexagonal R-3 structure. All calculations were performed using: SMART software for data collection; SAINT plus program¹ for integration and scale correction of data; SHELXTL¹ to resolve and refine.
the structure and to prepare material for publication; and ATOMS\(^3\) for molecular
graphics.
Compound 1 has an interstitial O\(^2-\) anion in the center of the Ln-octahedral arrangement,
acting as a template to induce the self-assembly of lanthanide ions. In our case, in order
to accomplish the electroneutrality of the molecule, one of the coordinated oxygen
species located on the 3-fold axes (O4, see Fig. 1) should be an OH\(^-\) group, while the
centrosymmetrically related one should be an O\(^2-\) anion. In this way, the H atom of the
OH- group would be the only atom that breaks the centrosymmetry of the structure.
Taking this into account, we performed the structure resolution and refinement in the
R3 space group. However, as in the case of the R-3 S. G., it was impossible to locate
such hydrogen atom, suggesting that a positional disorder occurs. The corresponding
wR\(_2\) and R\(_1\) index values were worse in the acentric space group and the H-atoms of the
half coordinated water molecules were not localized. In this way, we consider that the
more appropriate space group for 1 is the R-3 due to the fact that the non-localizable H
atom of the disordered OH\(^-\) group has such a small electron density that it cannot
effectively break the symmetry of the inversion center. The resultant formula of the new
compound must be [Sc\(_7\)(croc)\(_6\)(H\(_2\)O)\(_6\)(OH)\(_7\)O]\cdot4H\(_2\)O in order to satisfy the charge
balance.

**Characterization**
Fourier transform infrared spectra (FT-IR) was collected on a Nicolet 20SXC
spectrophotometer in the range 4000-250 cm\(^{-1}\), and KBr was used to prepare pellets of
the analyzed compounds.
Thermogravimetric and differential thermal analyses (TGA/DTA) were performed using
a SEIKO TG/DTA 320 apparatus in the temperature range 25–900 °C in air atmosphere
(flow of 100 mL/min) at a heating rate of 10 °C/min.
Field-emission scanning electron microscopy (FE-SEM) images were taken with a FEI
NOVA NANOSEM230 microscope with an accelerating voltage of 5-15 kV.
Figure S1. a) Infrared spectrum in the 4000-300 cm$^{-1}$ range, b) zoom in the 3700-3000 cm$^{-1}$ zone showing the deconvolution of the band using two independent Gaussian functions, in blue are plotted the experimental curve and in red the fitted one (inset are gathered the reliability factors of fit and curves parameters).
**Figure S2.** Asymmetric unit of the scandium croconate compound.

**Figure S3.** TG/DTA curves of the scandium croconate compound.
Figure S4. XRD Powder patterns of the scandium croconate compound: a) simulated, b) as synthetized by the second synthesis procedure, c) partially dehydrated.

References