Supporting Information

Experimental Section

General Synthesis Procedure

All reagents were purchased at high purity (AR grade) from AlfaAesar (croconic acid, $C_5O_5H_2$) and Strem Chemicals $Sc(CH_3CO_2)_3{\cdot}H_2O$ and were used without further purification.

The compound 1, with formula $[Sc_7(croc)_6(OH)_7(H_2O)_6O]{\cdot}4H_2O$, can be prepared by hydrothermal reaction of 0.25 mmol of $Sc(CH_3CO_2)_3{\cdot}H_2O$ with 0.375 mmol of the ligand ($C_5O_5H_2 = H_2croc$) 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 ºC 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 º in θ), using a *Bruker APEX2* software suite (each exposure of 10s covered 0.5 º in ω). Unit cell dimensions were determined by a least-squares fit of reflections with $I > 2\ \sigma(I)$. Data were integrated and scaled using *SAINTplus* program[1].

Unit cell dimensions were determined by a least-squares fit of reflections with $I > 2\ \sigma(I)$. A semi-empirical absorption and scale correction based on equivalent reflection was carried out using *SADABS*[1]. Space group determinations were carried out using *XPREP*[2]. 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* program[1] for integration and scale correction of data; SHELXTL[1] 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 refinenment 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 apropriate 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 $[Sc_7(croc)_6(H_2O)_6(OH)_7O]\cdot 4H_2O$ 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.

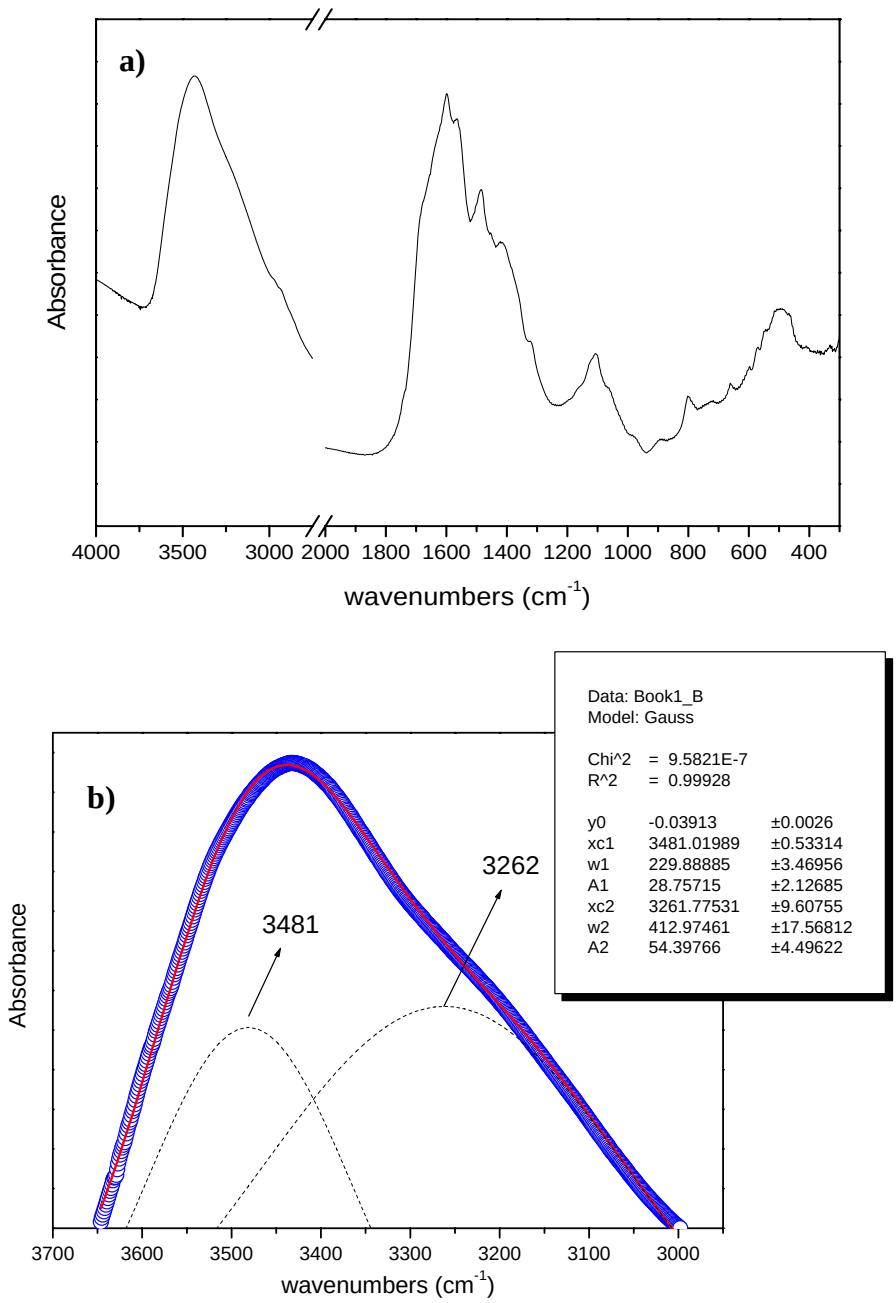

Figure S1. a) Infrared spectrum in the 4000-300 cm^{-1} range, b) zoom in the 3700-3000 cm^{-1} zone showing the deconvolution of the band using two independent Gaussian functions, in blue are plotted the experimental curve and in red the fitted one (inset are gathered the reliability factors of fit and curves parameters).

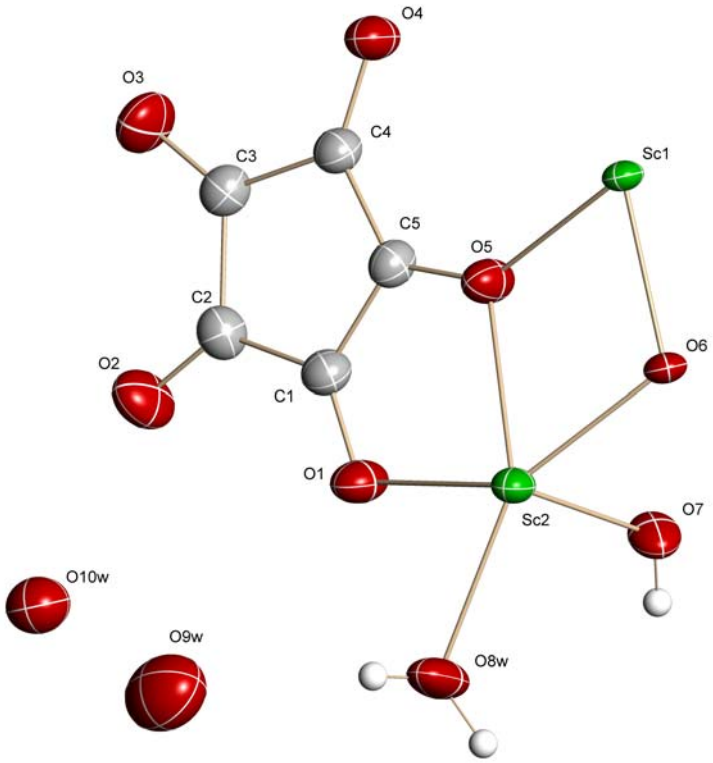

Figure S2. Asymmetric unit of the scandium croconate compound.

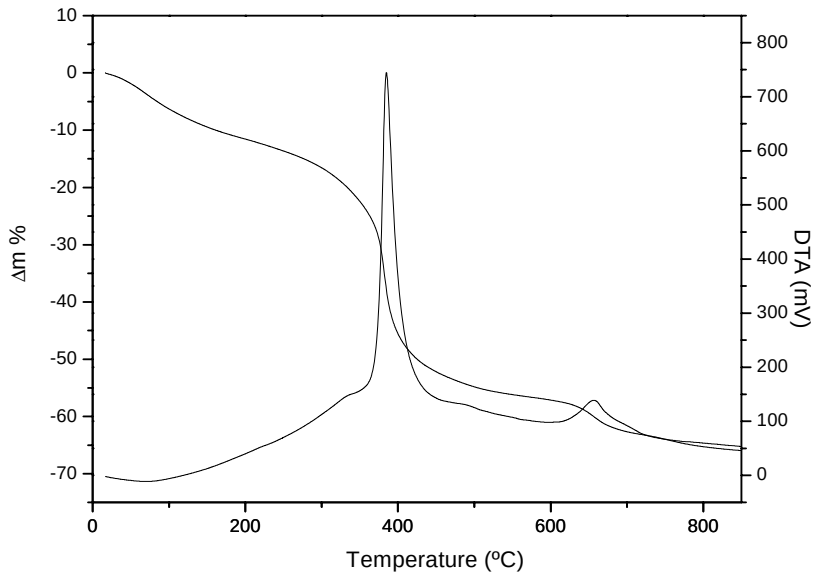

Figure S3. TG/DTA curves of the scandium croconate compound.

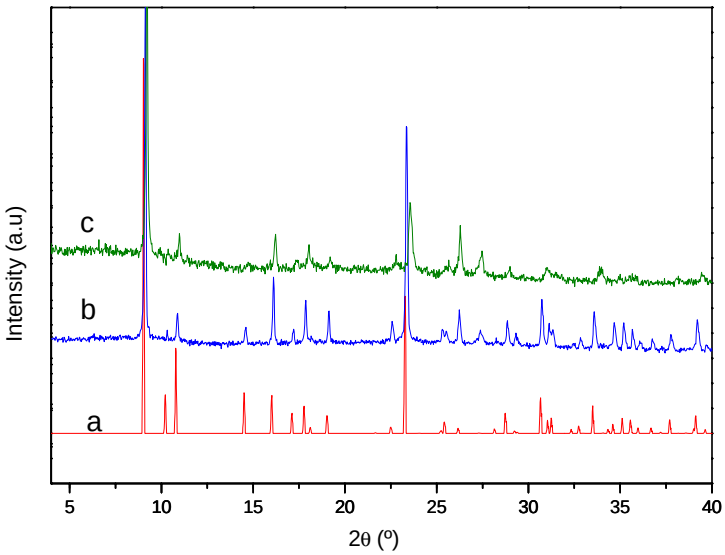

Figure S4. XRD Powder patterns of the scandium croconate compound: a) simulated, b) as synthetized by the second synthesis procedure, c) partially dehydrated.

References

[1] Siemens SAINT data collection and procedure software for the SMART system, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995.

[2] Siemens SHELXTL, version 5.0, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995.

[3] E. Dowty, ATOMS for Windows 3.1, a computer program for displaying atomic structure, Kingsport, TN, 1995.