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Synthesis, characterization, luminescent properties and theoretical study of two new coordination polymers containing lanthanide [Ce(III) or Yb(III)] and succinate ions

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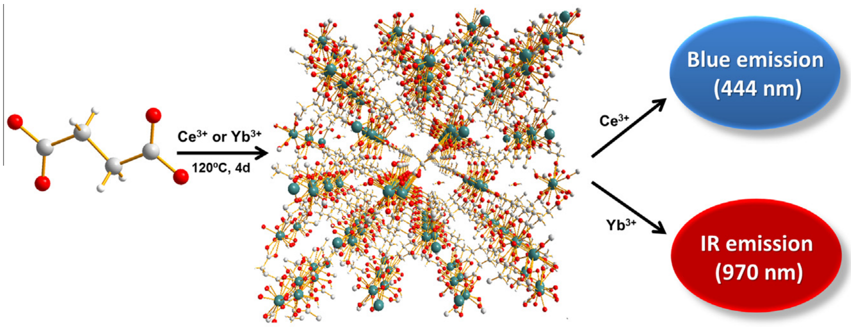
HIGHLIGHTS

- Novel Ce^{3+} and Yb^{3+} MOFs were obtained and the luminescent properties were studied.
- The same reaction conditions leads to two isostructural compounds.
- The emission bands were in 444 nm for Ce^{3+} ion and 970 nm for the Yb^{3+} ion.
- The SPARKLE/PM3 showed good accuracy to predict experimental structures.

GRAPHICAL ABSTRACT



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ABSTRACT

Two new three-dimensional coordination polymers $[Ce_2(C_4H_4O_4)_3(H_2O)_2]_n \cdot H_2O$ **1** and $[Yb_2(C_4H_4O_4)_3(H_2O)_2]_n \cdot H_2O$ **2** have been synthesized under hydrothermal conditions and characterized by single-crystal X-ray, elemental, infrared and thermogravimetric analysis. Both compounds crystallized in the monoclinic system and space group *C2/c* with cell parameters $a = 20.1178(2)$, $b = 7.98150(10)$, $c = 14.03090(10)$, $\beta = 120.9050(10)$, cell volume = 1933.07(3) Å^3 for **1**, and $a = 19.7360(3)$, $b = 7.59790(10)$, $c = 13.7564(2)$, $\beta = 121.3060(10)$, cell volume = 1762.47(4) for **2**. The solid-state structures of the two metal–organic frameworks (MOFs) were subjected to detailed analysis using the semiempirical Sparkle/AM1, Sparkle/PM3 and Sparkle/PM6 quantum models. The theoretical results obtained were in good overall agreement with the experimental data, although the Sparkle/PM3 model presented the highest accuracy. The luminescent spectra of **1** and **2** showed emission bands characteristic of the Ce (III) and Yb (III) at 444 nm and 970 nm, respectively. Thermal analysis revealed that both MOFs lost one molecule of water of hydration and two molecules of coordinated water upon heating. In compound **1**, the removal of water occurred in two steps while in **2**, water loss occurred in a single step.

1. Introduction

In the field of the solid state chemistry, structures so called metal–organic frameworks [1,2] have been studied due to applications in strategic areas such as gas storage and catalysis [3]. The succinates ions are interesting ligands, once they have carboxyl groups able to coordinate with metal cations and their flexible organic chains leads different conformations, as reported in literature [4]. This combination (conformation + coordination mode) is a powerful tool, and due to this, the succinates ligands are often employed in syntheses of MOFs with d-transition [5] and lanthanides metals [1].

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Metal–organic frameworks (MOFs) containing lanthanide ions have been investigated extensively in recent decades by virtue of the interesting range of applications that they offer and their tendency to form high quality crystals that are appropriate for X-ray crystallographic studies [1,6–17]. The reactions of lanthanide ions with succinic acid are very sensitive to changes in synthetic conditions and the complexes so-produced exhibit considerable structural diversity, typically comprising three-dimensional (3-D) networks with monoclinic or triclinic crystal systems. Lanthanide succinate has shown interesting catalytic properties in reactions such as sulfides oxidations and aldehyde acetalization [7].

In the case of cerium ions, Seguatni et al. [8] published the synthesis of a succinate of Ce by hydrothermal method at 200 °C and obtained a coordination network $[Ce_2(C_4H_4O_4)_3(H_2O)_2]$ without water hydration. Other succinate $[Ce(C_4H_4O_4)(H_2O)_4 3H_2OCl]_n$ containing coordinated Cl atoms has been synthesized by grown phase under reflux [6]. MOFs with ytterbium and succinic acid have been prepared by hydrothermal reaction with triethylamine (pH 3.5) for 90 h at 180 °C [1]. The Yb-succinate comprised a triclinic crystal system and exhibited a reversible temperature-triggered single-crystal to single-crystal transformation when heated to ≈180 °C.

In addition to experimental studies, computational models have been used to predict many physical and chemical properties of the coordination compounds. For lanthanide complexes, our group has shown the potential of Sparkle mode [18–20] to calculate the ground state geometries of these systems with high accuracy [21]. Currently the majority of studies using Density Functional Theory – DFT to the quantum chemical calculation of structures solid phase. In these calculations, to allow the study of systems with a high number of atoms single DFT potentials are used. This methodology considers the conditions of periodicity of the solid phase by the addition of translational vectors at the coordinates of geometrical systems. Recently, Stewart published a similar procedure [22] in order to perform calculations using solid phase semiempirical methods. Although the procedure has been proposed for the model PM6 [23], tests indicate that the use of similar models as the AM1 [24] and PM3 [25,26] are also feasible RM1 [27] maintaining the level of accuracy. For all we know, the application of this procedure associated with the Sparkle model for the study of MOFs containing trivalent lanthanide ions is only found in two articles published in 2012 [28] and 2013 [17] by our group. Although the results have been interesting and have shown good accuracy compared to experimental data further investigation should be conducted seeking to validate this approach, mainly by applying different Sparkle models (Sparkle/AM1 [18], Sparkle/PM3 [19] and Sparkle/PM6 [20].

In the present work we report herein the synthesis and characterization of two new 3-D coordination polymers comprising succinate ions and Ce or Yb. The ion Ce^{3+} is important element of lanthanide series that has $4f^1$ configuration and is, therefore, capable of producing luminescence from red region until UV-region due to strong crystal field dependence of its 5d–4f transition energy. Already Yb^{3+} ion has a single line emission in the range of 980–1030 nm, due to its extremely simple structure electronics with an unpaired electron. To validate the procedure proposed by Stewart for solid state calculations in association with the semiempirical Sparkle model we used semiempirical Sparkle/AM1, Sparkle/PM3 and Sparkle/PM6 models to calculate the ground state geometries of the MOFs and compared with the crystallographic structures.

2. Materials and methods

2.1. Materials

The oxides of Ce and Yb (purity > 99%) were purchased from Sigma–Aldrich and used as received; all other chemicals were of AR grade. Hydrated Ce(III) chloride and Yb(III) chloride were obtained by reaction of the respective oxides with concentrated hydrochloric acid [29].

2.2. Synthesis of lanthanide succinates

Succinic acid (0.059 g, 0.5 mmol) was dissolved in 10 mL of water contained in a Teflon-lined stainless steel reactor and the pH of the solution was adjusted to 5 with 2 M sodium hydroxide. $LnCl_3 \cdot xH_2O$ (0.5 mmol, Ln = Ce or Yb) was added to the reaction mixture and the reactor was sealed and maintained at 120 °C for 4 days. After this time, the reactor was allowed to cool slowly to room temperature and crystalline needles of **1** and **2** were isolated by filtration, washed with water and dried in the air. The yield of **1** (based on ligand) was 28.17%. Elemental analysis for $C_{12}H_{18}O_{15}Ce_2$ (**1**): calcd. (%) C 21.10, H 2.64; found (%) C 20.67, H 2.75. The yield of **2** (based on Yb) was 85.07%. Elemental analysis for $C_{12}H_{18}O_{15}Yb_2$ (**2**): calcd. (%) C 19.25, H 2.41; found (%) C 19.35, H 2.50.

2.3. Physical measurements

Infrared spectra (4000–400 cm^{-1}) were recorded on a Bruker model FS66 FT-IT spectrophotometer with the analytes dispersed in KBr pellets. The excitation and emission spectra were measured at room temperature on an ISS model PC1 spectrofluorimeter fitted with a photomultiplier: the excitation monochromator was equipped with a 300 W xenon lamp and the emission was collected in a monochromator with a resolution of 0.1 nm. Thermogravimetric analyses were performed on a Shimadzu model DTG-60H thermal analyzer with a heating rate of 10 °C/min to 900 °C and a N_2 flow rate of 50 mL/min.

2.4. Determination of crystal structure

Single crystals of compounds **1** and **2** were selected for X-ray diffraction. Intensity data were collected at room temperature (298 K) using an Enraf Nonius KappaCCD diffractometer with CCD [30] detector and Mo Kα monochromatic radiation (λ = 0.71073 Å). The crystal structures were solved by direct methods and refined anisotropically by full matrix least squares on F^2 values. All of the H atoms attached to C atoms were located on stereochemical grounds and refined with fixed bond lengths and angles, each riding on a carrier atom, with an isotropic displacement parameter of 1.2-times the value of the equivalent isotropic displacement of the atoms to which they were bound. Significant absorption effects were observed for compounds **1** and **2**, and absorption corrections were applied [31]. The final model showed a discrepancy of 0.0159 [$R_{(all)}$ = 0.0172] and goodness of fit (GOF) = 1.058 for **1**, and of 0.0148 [$R_{(all)}$ = 0.0170] and GOF = 1.079 for **2**.

The software employed in the determination of crystal structures were: COLLECT [30] for data collection, DENZO and SCALEPACK [32] for data analysis, SHELXS-97 [33] for structure solution, and SHELXL-97 [34] for structure refinement. The program ORTEP-3 [35] was employed for the construction of molecular graphics and WinGX [36] was used to prepare material for publication. The crystallographic data and details of the structural analyses are summarized in Table 1. The cif data files have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with reference numbers 919696 and 919697.

2.5. Theoretical study

The semiempirical Sparkle/AM1 [37,38], Sparkle/PM3 [39,40] and Sparkle/PM6 [20] models were employed in the calculation of the ground state geometries of the MOFs. Geometric and crystallographic parameters were used to evaluate the accuracy of the