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Short Note

Synthesis, Structural Characterization, and SHG Behavior of a Lanthanum/ β -D-Fructose-Based Metal Organic Framework

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Abstract

Interest in non-centrosymmetric crystalline materials exhibiting second harmonic generation (SHG) has increased due to their potential applications in optical sensing and biosensing. Saccharide-based metal complexes are particularly attractive systems, as chiral sugars can promote non-centrosymmetric crystal packing. In this work, a new lanthanum- β -D-fructose compound, $[\text{La}(\text{C}_6\text{H}_{12}\text{O}_6)(\text{H}_2\text{O})_5]\text{Cl}_3$ (LaFRUCl), was synthesized by a simple and low-cost method and characterized by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ and consists of infinite $(\text{La}^{3+}\text{-fructose})_n$ chains extending along the [001] direction, forming a one-dimensional metal-organic framework. The nonlinear optical response was evaluated using the Kurtz-Perry powder technique with a Nd:YAG laser (1064 nm) and compared to a sucrose reference. The measured SHG efficiency is comparable to that of previously reported alkaline earth metal-sugar analogues. While the SHG emission is significant, evaluation of the compound's structural stability under aqueous or physiological conditions would be required before considering biological applications.

Keywords: non-linear optical properties; second harmonic generation; metal organic framework; lanthanum-carbohydrate derivative

1. Introduction

Interest in materials with Non Linear Optical (NLO) properties, and in particular Second Harmonic Generation (SHG), for use as biosensors has increased significantly over the years, thanks to several advantages over fluorescence-based method [1–5]. The enhanced sensitivity of SHG detectors allows for the exploration of a wide range of compounds having low SHG emission but high biocompatibility [6,7].

The most critical requirement for a crystalline material to exhibit SHG properties is the absence of a center of inversion in its structure. Low-cost chiral saccharide molecules, when incorporated into crystals with other substances, effectively induce this non-centrosymmetry [8]. For many years, our research has focused on metal complexes with saccharide ligands; these are biocompatible materials and show significant SHG emission, making them good candidates for SHG bio-sensing.

We analyzed the SHG behavior of compounds featuring various alkaline earth metals (Ca^{2+} , Sr^{2+}), different sugars (D-fructose, D-ribose, 2-deoxy-D-galactose) and various counterions (Cl^- , Br^- , I^-). We also had the opportunity to study isomorphous structures, Metal Organic Frameworks (MOFs), and molecular crystals [9,10], and references therein. Given that the crystal structure is the primary factor influencing SHG emission of this class of compounds, we observed that heavier anions generally have a significant influence on SHG intensity, while heavier cations also contribute, albeit to a lower extent. In this context, we decided to investigate an analogue compound containing a very heavy

metal, Lanthanum, to evaluate the effect of a heavier and more polarizable metal center on SHG efficiency.

In this work, a new β -D-fructose-lanthanum complex with the formula $[\text{La}(\text{C}_6\text{H}_{12}\text{O}_6)(\text{H}_2\text{O})_5]\text{Cl}_3$ (LaFRUCl) was synthesized and characterized by single crystal X-ray diffraction (XRD). Its SHG response was measured with a Nd:YAG pulsed 1064 nm laser and compared with analogue metal-sugar-based from our previous studies.

2. Results and Discussion

The synthesis of the LaFRUCl compound involves a simple, rapid, low-cost, and environmentally benign method in which the sugar and the metal salt were mixed in an alcoholic solution, and the product precipitates during the slow evaporation of the solvent. This method exploits the natural capacity of hydroxyl groups of the sugar to coordinate with the lanthanum ion. The product precipitates, forming directly high-quality crystals for X-ray diffraction.

X-ray diffraction characterization confirms the non-centrosymmetric structure ($P2_12_12_1$), as expected from the intrinsically chiral fructose ligand, which results in an asymmetric coordination environment around the lanthanum(III) center.

The asymmetric unit of LaFRUCl consists of one La^{3+} ion, one fructose molecule, five water molecules coordinated to the metal center, one lattice water molecule, and three free chlorine anions (Figure 1). The fructose molecules bridge two metal cations using all their hydroxyl groups, forming infinite $(\text{La}^{3+}\text{-fructose})_n$ chains (Figure 2) extending along the $[001]$ direction. Consequently, the structure can be described as a 1D Metal-Organic Framework (MOF).

The chlorine atoms are positioned between these chains, stabilized by a network of strong hydrogen bonds involving the hydroxyl groups of the fructose and both the coordinated and lattice water molecules (see Figure 2). A list of the most significant hydrogen bonds in the structure is provided in Table S4 of the Supporting Information.

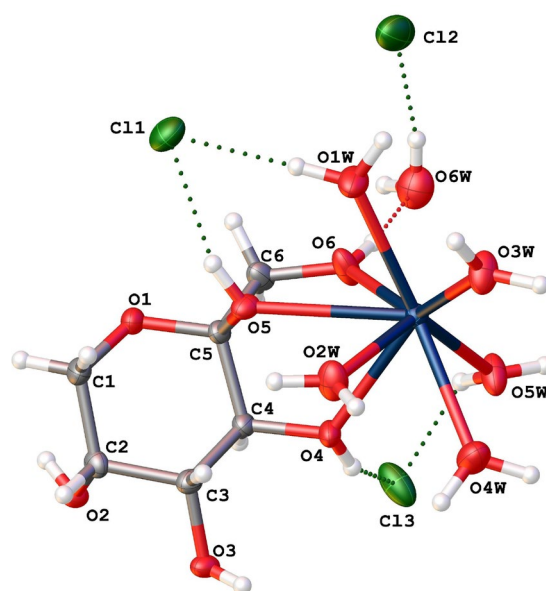


Figure 1. View of the asymmetric unit of LaFRUCl with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

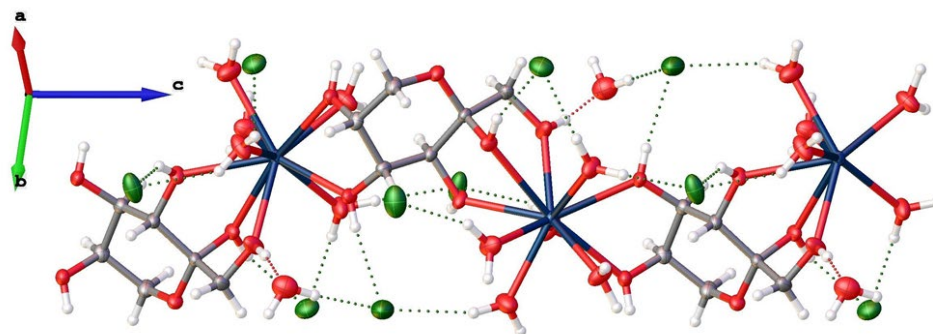


Figure 2. View of the packing motif of LaFRUCl viewed along the [001] direction.

The SHG response of the compound was measured on a powder sample, hand-ground in an agate mortar. The powder was loaded in a capillary tube, and the SHG intensity was measured relative to a sucrose standard under the same experimental condition. The $I^2_w/I^2_{w,sucrose}$ value recorded for LaFRUCl was 0.64. This value is consistent with the average magnitude observed for analogous compounds based on Ca, Sr, Cl, or Br combined with D-fructose, 2-deoxy-D-galactose, or D-ribose [10]. Consequently, the presence of the lanthanum ion did not result in the expected enhancement of SHG efficiency.

3. Materials and Methods

Lanthanum chloride heptahydrate and β -D-fructose were purchased from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany) and used without additional purification.

3.1. Synthesis of $[La(C_6H_{12}O_6)(H_2O)_5]Cl_3$ (LaFRUCl)

Lanthanum chloride heptahydrate and β -D-fructose powders were mixed in a 1:1 stoichiometric ratio and ground in an agate mortar. During grinding, the reagents began to react, partially due to ambient humidity, as evidenced by the formation of a sticky material. XRPD patterns confirmed the amorphous nature of this intermediate. The resulting solid was partially dissolved in few drops of ethanol, and the solution was maintained in equilibrium with the solid for one week. Colorless crystals suitable for the XRD analysis formed on the vial walls. These were briefly washed with ethanol and dried in an oven at 323 K.

3.2. Single Crystal X-Ray Diffraction (XRD) of LaFRUCl

X-ray diffraction data were collected at room temperature using a Xcalibur AtlasS2 Gemini R Ultra diffractometer equipped with graphite monochromatized Mo-K α radiation (0.71073 Å). The CrysAlisPro [11] package was used for data collection and integration. The structure was solved using SHELXT [12], refined with SHELXL [13] and Olex2 [14] was used for graphics.

Crystal data: Orthorhombic, space group $P2_12_12_1$, $Z=4$, $a= 10.0145(2)$, $b= 12.3587(3)$ Å, $c= 14.9211(3)$, $V= 1846.74(7)$ Å³. A total of 22876 reflections were collected. of which 5637 were unique ($R_{int}=0.0467$). Final refinement indices: $R1=0.0288$ ($I>2\sigma(I)$), $wR2=0.0607$ (all data).

All non-hydrogen atoms were refined with anisotropic displacement parameters. Although hydrogen atom positions were visible in the difference Fourier maps, they were placed in calculated positions and refined using a riding model with the $U_{iso}=1.2$ or $1.5 \times U_{eq}$ of the parent atom. The interested reader can find further details on crystal data, data collection, least-squares refinements, and bond lengths and angles in the Supporting Information (Tables S1-S3) and CIF file (CCDC 2240232).

3.3. Second Harmonic Generation Measurements

The SHG efficiency was determined by the Kurtz–Perry powder technique, using a nanosecond Nd:YAG pulsed (10 Hz) laser with fundamental 1064 nm. The SH signal generated by ground samples in capillary tubes was collected by an elliptical mirror, detected by a photomultiplier, and compared to the ground sucrose signal collected under the same conditions (sucrose displays an SHG equal to 0.7 that of KDP).

4. Conclusions

In this work, a new lanthanum/fructose-based MOF, $[\text{La}(\text{C}_6\text{H}_{12}\text{O}_6)(\text{H}_2\text{O})_5]\text{Cl}_3$, was synthesized with a simple and low-cost method, and structurally characterized by single-crystal X-ray diffraction. The compound crystallizes in the non-centrosymmetric orthorhombic space group $\text{P}2_12_12_1$ and consists of infinite $(\text{La}^{3+}\text{--fructose})_n$ chains extending along the [001] direction, which can be described as a 1D Metal–Organic Framework.

Second harmonic generation measurements performed using the Kurtz–Perry powder technique revealed an SHG efficiency comparable to that of previously reported alkaline earth metal–sugar analogues indicating that the introduction of the lanthanum ion does not result in a significant enhancement of SHG intensity. Although the SHG response is significant enough for potential use as a biosensor, further studies on stability and potential metal ion release would be required before considering biological applications.

Supplementary Materials. The following supporting information can be downloaded at the website of this paper posted on Preprints.org. Table S1. Details on crystal data and structure refinement for LaFRUCl; Table S2. Bond Lengths for LaFRUCl; Table S3. Bond Angles for LaFRUCl; Table S4. List of stronger hydrogen bonds for LaFRUCl; CIF file.

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Data Availability Statement: The crystallographic data for this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC 2240232). These data can be obtained free of charge via www.ccdc.cam.ac.uk/structures/. Additional data supporting the findings of this study are available from the corresponding author upon reasonable request. .

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Conflicts of Interest: The authors declare no conflicts of interest.

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