



Crystal structure and characterization of a novel luminescent 2D metal-organic framework, poly[aquaitaconatocalcium(II)] possessing an open framework structure with hydrophobic channels

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ABSTRACT

A novel 2D metal-organic framework poly[aquaitaconatocalcium(II)] with an open framework structure has been successfully grown by single gel diffusion technique. Sodium metasilicate was used for gel preparation. The structure was determined by single crystal X-ray diffraction. The compound crystallizes in monoclinic space group $P2_1/c$ with hydrophobic 1D channels. The obtained crystals were further characterized by elemental analysis, FT-IR and UV-Visible spectroscopy, powder X-ray diffraction and thermogravimetry. The luminescent property of the complex was also discussed.

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1. Introduction

Metal-organic frameworks derived from metal ions and organic ligands have emerged as an important family of porous materials with intriguing new structural topologies and potential applications in a wide variety of fields [1–6]. Owing to the conformational freedom of flexible multicarboxylates, these are often employed for the construction of frameworks with unique structure and useful properties [7–10]. Itaconic acid (IA) or methylene succinic acid, an aliphatic dicarboxylic acid, is a very cheap and an excellent flexible ligand. IA has the ability to bind through both carboxylate end groups and can exhibit extensive variety of coordination modes. IA can form interesting structural motifs because of its extended character and binding ability. Itaconic acid is a promising compound for the production of alternative biofuels chemicals and elastomers. Based on its industrial potential, it was selected by U.S Department of Energy as one of the top 12 building block

chemicals to produce from biomass. IA can display as many as ten different coordination modes [11]. This interesting feature of IA and the relatively unexplored structural chemistry of its metal complexes prompt us for the present study. We focus on alkaline earths which have received only less attention despite its potential applications. Non-toxic, solubility in aqueous media, variable structural chemistry, affinity for O-donor ligands and biological applications are some of the important factors responsible for the current interest in the chemistry of alkaline earths [12]. Among alkaline earth metals, coordination compounds based on Ca(II) ion are particularly interesting because Ca(II) ion lacks d orbital electrons and can show higher coordination numbers ranging from six to nine [13].

In the present investigation, we have grown single crystals of poly[aquaitaconatocalcium(II)] (PAIC) by gel diffusion technique at room temperature. To the best of our knowledge, this is the first report of the title compound. The structure of the compound was determined from the single crystal X-ray diffraction studies. The crystals obtained were characterized by elemental analysis, FT-IR and UV-Visible spectral studies, powder X-ray diffraction and thermogravimetry. The luminescent property of the ligand and the complex were also investigated.

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Fig. 1. Photograph of crystalline PAIC.

Table 1
Percentage composition of C and H of PAIC.

| Element | Experimental (%) | Theoretical (%) |
|---------|------------------|-----------------|
| C | 32.27 | 32.23 |
| H | 3.45 | 3.22 |

2. Experimental

2.1. Growth procedure

Single gel diffusion technique was used for growing quality crystals of PAIC [14]. Gel method is found to be a simple strain free method for producing perfect crystals with high optical perfection and wide morphology at room temperature. Silica hydro gel prepared from an aqueous solution of sodium metasilicate (SMS) ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) was employed for this purpose. Gel matrices were prepared in borosilicate glass tubes. SMS solution taken in these glass tubes was acidified with aqueous itaconic acid of desired molarity (0.2–1 M) till a desired pH was obtained. The glass tubes were then left for setting. After ensuring proper gelation, calcium nitrate solution of desired molarity (0.2–1 M) was carefully poured over the set

gel without tampering the gel meniscus. The glass tubes were well sealed with plastic sheets to eliminate surface contamination.

2.2. Physical measurements

The elemental analysis of the grown crystals was carried out using Elementar Vario-EL 111 CHNS analyzer. The FT-IR spectrum was recorded using potassium bromide pellets on a Thermo Nicolet, Avatar 370 spectrometer in the range $4000\text{--}400\text{ cm}^{-1}$. Powder X-ray diffraction studies were carried out using a Bruker AXS D8 advance XRD with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056\text{ \AA}$). The optical absorption spectrum of the pure solid was recorded using Varian Cary 5000 UV–Vis–NIR spectrometer in the range $200\text{--}1200\text{ nm}$. The thermal analysis of the crystals was carried out using a Perkin Elmer Diamond TG/DTG analyzer instrument with a heating rate of $10\text{ }^\circ\text{C/min}$ in nitrogen atmosphere. The photoluminescence spectrum of the ligand and the complex was recorded using JY Horiba PL metre at room temperature.

The single crystal X-ray diffraction study of the grown crystal PAIC was recorded using a Bruker AXS Kappa Apex2 CCD diffractometer at room temperature with graphite monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073\text{ \AA}$) radiation. The unit cell dimensions and intensity data were recorded at 293 K. The program SAINT/XPREF was used for data reduction and APEX2/SAINT for cell refinement [15]. The structure was solved by SIR92 and refined by full-matrix least squares on F^2 using SHELXL-97 computer programs [16,17]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Carbon-bound H-atoms were placed in calculated positions and included in the refinement in the riding model approximation. The hydrogen atoms of the coordinated water molecule were located in a difference Fourier map and refined isotropically. DIAMOND software version 3.1f was employed for structure plotting [18].

3. Results and discussion

3.1. Crystal growth

Transparent, well faceted crystals of PAIC appeared at the gel interface after one week and the growth was completed within two weeks. Several batches of experiments corresponding to different densities of the gel ($1.02\text{--}1.06\text{ g cm}^{-3}$) and the pH values (5–7.5) were conducted and the optimum conditions for crystal growth are: concentration of IA = 1 M, concentration of calcium nitrate

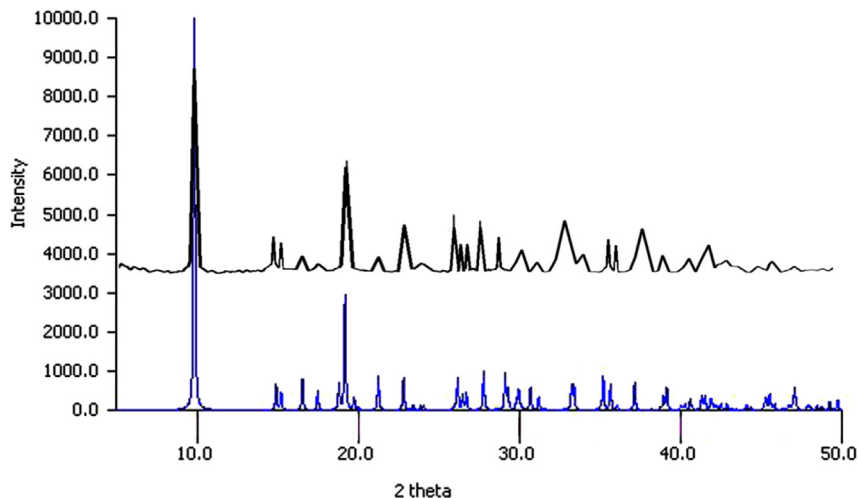


Fig. 2. Experimental and simulated X-ray diffractogram of PAIC.

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