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Growth and characterisation of a new polymorph of barium maleate: A metal organic framework

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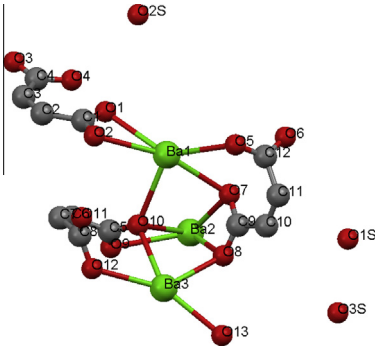
HIGHLIGHTS

- Metal co-ordination complexes of dicarboxylic acids have a wide range of potential applications.
- Single crystals of a new polymorph of barium maleate (BM) are grown by modified gel method.
- Two dimensional polymeric BM structure is stabilized by intermolecular hydrogen bonds.
- FT-IR studies and TGA/DTA studies are performed on the sample.
- The optical transparency of BM makes it attractive for optoelectronic applications.

GRAPHICAL ABSTRACT



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ABSTRACT

A new polymorph of barium maleate (BM) with chemical formula $C_{24}H_{14}O_{24}Ba_5{\cdot}7H_2O$ is grown by modified gel method. Transparent plate like crystals of dimensions $9 \times 4 \times 1$ mm^3 were obtained. Single crystal X-ray Diffraction analysis was done to determine the structure and the crystal belongs to triclinic system, *P-1* space group with cell dimensions $a = 7.2929(3)$ Å, $b = 10.5454(4)$ Å, $c = 14.2837(6)$ Å, $\alpha = 102.0350(10)°$, $\beta = 99.1580(10)°$, $\gamma = 102.9170(10)°$. Hydrogen bonding stabilises the two dimensional polymeric crystal structure. Fourier Transform Infrared spectroscopic method was utilised for the analysis of various functional groups present in the complex. Elemental analysis confirmed the stoichiometry of the complex. Thermal properties of the crystal were studied by TGA/DTA. The material melts at 368 °C. The optical transparency of the crystal was studied using UV–Visible absorption spectra. The optical band gap is found to be 3.35 eV.

Introduction

Metal co-ordination complexes of dicarboxylic acids are of extensive research interests due to their wide range of potential applications in polymer industry, drug design, optoelectronic industry, gas storage, etc. The co-ordination complexes of various transition and rare earth metals with interesting properties are reported [1–3]. Maleic acid (cis-butenedioic acid) is a dicarboxylic acid which is widely used in the production of synthetic resins and as an intermediate in the production of other chemicals. Chemistry of maleic acid and the availability of monomers in a cheaper rate

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help to synthesize maleic acid polymer easily. Biocompatibility, water solubility and generally well-defined structure of maleic copolymers suit them to be used in a variety of medical and pharmaceutical applications [4]. It is one of the biologically important dicarboxylic acids and its interaction with different metal ions opens new potentialities with targeted properties. Barium, an alkaline earth metallic element, is used in fireworks, glass making, etc. Barium meal is medicinally used as X-ray contrast media. The electronic industries use barium based getters to remove traces of gases from cathode ray tubes, vacuum tubes and heat pipe solar collectors [5]. Barium salt of maleic acid is used in the catalysis process of hydrocarbon steam reforming [6].

Herein we report a new polymorph of barium maleate grown by modified gel method. The BM crystals grown by the conventional gel method provides the same structure as that of the reported one, while the introduction of neutral gel layer in our experiment provides a new polymorph of barium maleate belonging to the triclinic system [7]. Single crystal XRD analysis, Fourier Transform (FT) infrared technique, UV–Visible spectral studies, thermo-gravimetric analysis and differential thermal analysis were used for the crystal characterisation.

Experimental procedure

Crystallisation method

The crystallisation of the barium complex of maleic acid was accomplished using modified gel diffusion technique. Good quality single crystals were obtained by controlled nucleation and convection less growth offered by gel technique. Crystals were grown in single glass tube of length 20 cm and diameter 2.5 cm. Silica gel of specific gravity 1.03 to 1.06 g/cc was prepared by dissolving sodium meta silicate (SMS) in double distilled water. Maleic acid of particular molarity (0.5–1.5 M) was added drop by drop to the continuously stirred SMS. The gel was then acidified with 1 M glacial acetic acid to get pH in the range 3–7. About 30 ml of above solution was taken in each test tube and kept undisturbed for setting. Over the set gel, a neutral gel layer (pH-7) was introduced without disturbing it. Aqueous solution of barium chloride (0.5 M –1.5 M) was added as top reagent over the set neutral gel without damaging the gel system. The open end of the test tubes was covered with transparent plastic sheets to avoid contamination of the solution. The experimental set up was kept undisturbed for crystallisation at ambient temperature.

Characterisation

The single crystal XRD analysis of the crystal was carried out using Bruker AXS Kappa Apex2 CCD diffractometer. FT-IR spectrum was recorded using KBr pellets on a Thermo Nicolet, Avatar 370 spectrometer with resolution of 0.9 cm^{-1}, in the range 4000–400 cm^{-1}. Absorption spectrum of the crystals was studied using Varian Cary 5000 UV–Vis NIR spectrometer in the range 200–1200 nm. TGA/DTA experiments were carried out in SDT Q600 V8.3 Build 101 instrument with a heating rate of 10 °C/min in nitrogen atmosphere. The carbon and hydrogen contents in the sample were determined using Elementor Vario-EL III CHNS Analyser.

Results and discussion

Crystal growth

Crystals of BM were grown as per the crystal growth technique described in Section 'Crystallisation method'. The experiment was first started with the conventional gel method with maleic acid impregnated in the gel with barium chloride as top solution, which provided crystals in the form of whiskers. To get perfect single crystals for structural elucidation, a neutral gel layer was added above the set gel. Top solution was gently poured over the set neutral gel layer. Tiny crystals were first sighted at the neutral gel region on the fourth week. Rectangular shaped single crystals were obtained in the neutral gel layer in the pH range 5–5.5. The addition of intermediate neutral gel slowed down the diffusion of barium chloride, reduced the nucleation sites, eliminated the formation of whisker like structures and produced transparent plate like single crystals. Growth process took about 3 months to complete. Good quality single crystals suitable for single crystal XRD studies were obtained in gel medium of pH 5.5, density 1.04 g/cc, 1 M maleic acid and 1 M barium chloride. Crystals of size $9 \times 4 \times 1$ mm^3 were obtained. The characteristic shape of the crystal is shown in Fig. 1.

Crystal structure

The single crystal XRD data of a well formed BM crystal were collected using Bruker AXS Kappa Apex2 CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. Data reduction was done using SAINT/XPREP program [8]. The program SIR92 was used for solving the crystal structure and the refinement was carried out by full-matrix least squares on F^2 using SHELXL-97 [9,10]. Anisotropic thermal parameters were applied to refine all the non-hydrogen atoms. The hydrogen atoms were located from the difference Fourier maps and refined isotropically. The IUCR software Mercury (Version 3) was used to construct molecular graphics. Table 1 provides the crystallographic data and processing parameters. Fractional atomic co-ordinates are given in Table 2.

The whisker shaped crystals formed in this work by the conventional gel method have the same unit cell parameters as that of the reported structure (a = 9.3721 Å, b = 20.5880 Å, c = 14.0744 Å and $\alpha = \gamma = 90°$, P 21/c) [7]. Here we are reporting a new polymorph of barium maleate crystallised using the modified gel method. The unit cell parameters and the crystal system of BM are entirely different from that of the reported one. Fig. 2 denotes the co-ordination environment of BM with atom numbering scheme. Barium in this structure exhibits 3 different co-ordination environments. Barium atoms are surrounded by oxygen atoms of maleic acid units. Ba1, Ba2, Ba3 have the co-ordination numbers 10, 12, 8 respectively while Ba in the reported structure is seven co-ordinated. The Ba—O bond length ranges from 2.672(3) Å to 2.989(2) Å. Selected bond lengths and bond angles are given in Tables 3 and 4 respectively. Taking the asymmetric unit, one of the carboxyl groups of maleate anion is chelated to Ba1 through

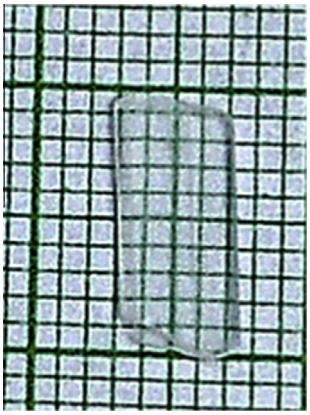

Fig. 1. Photograph of grown BM.