Growth and Characterisation of Gel Grown Lead Maleate

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***Abstract*—Lead maleate (PbM) crystals are grown by gel diffusion method for the first time. Optimization techniques are adopted to improve the crystal quality. Single crystal X-Ray Diffraction analysis was done to determine the structure. The crystal was found to be monoclinic with P21/C space group. Hydrogen bonding stabilizes the two dimensional polymeric crystal structure. Fourier Transform Infrared spectroscopic method was utilized for the analysis of various functional groups present in the complex. Thermal properties of the crystal were studied by TGA/DTA. Elemental analysis gives the formula of the compound as $PbC_2H_2(CO_2)_2$and confirmed the stoichiometry of the complex. The UV-Visible spectral analysis was used to study the optical transparency of the crystal.**

Key words: Crystal growth, SXRD, Lead maleate, FTIR, TGA/DTA.

I. INTRODUCTION

Metal Organic Frameworks (M.O.F.) of dicarboxylic acids have potential application in fields like catalysis, drug design, gas storage , nonlinear optics and chemical sensing because of their unique properties as well as structural diversity. Maleic acid (cis-butenedioic acid) is a dicarboxylic acid which is a multifunctional chemical intermediate that finds applications in nearly every field of industrial chemistry [1]. Maleic acid is extensively used in pharmaceutical industry for making maleate salts of drugs. Lead maleate is an active heat stabiliser for halogenated polymers[2]. It is used in wire insulation and jacketing.

M.O.Fs are produced mainly by hydrothermal or solvothermal techniques, where the crystals are slowly grown from hot solutions. A report on the growth of lead maleate from hot solution is available [2].Our attempt was to grow PbM at ambient temperature by the gel method and to reinvestigate the crystal structure. Here we report the growth and characterisation of lead maleate crystals by gel method for the first time. Gel method is an inexpensive, effective and unique method for growing defect free crystals showing poor solubility in water by providing the advantages of controlled nucleation and convection less growth at ambient temperature [3].The grown crystals are then subjected to Single Crystal XRD analysis for structure determination and further characterised by elemental, thermal, FTIR and UV-Visible spectral analysis.

II. EXPERIMENTAL PROCEDURE

A. Growth Procedure

The crystals of the lead complex of maleic acid weregrown using gel diffusion technique. Good quality single crystals were obtained by controlled nucleation and convection less growth offered by gel technique. Single glass tubes of length 20 cm and diameter 2.5 cm are used for the growth procedure. Silica gel of specific gravity 1.03 to 1.06 was prepared by dissolving sodium meta silicate (SMS) in double distilled water. Maleic acid of particular molarity (0.5 M – 1.5 M) was added drop by drop to the continuously stirred SMS. The gel was then acidified with 1M glacial acetic acid to get pH in the range 3 to 7. About 30 ml of above solution was taken in each test tube and kept undisturbed for setting. Aqueous solution of lead nitrate (0.5 M –1.5 M) was added as top reagent over the set gel without damaging the gel system. The experimental set up was kept undisturbed for crystallisation at ambient temperature.

B. Characterization

The crystals grown by gel method were subjected to various characterization studies.

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 0.9cm-1, in the range 4000-400cm-1. Absorption spectrum of the crystal was studied using Varian Cary 5000 UV-Vis-NIR spectrometer in the range 200-1200nm. TGA/DTA experiments were carried out using Perkin Elmer Diamond

TG/ DTG analyser with a heating rate of 10◦C/min in nitrogen atmosphere. The carbon, hydrogen, nitrogen and sulphur contents in the sample were determined using ElementorVario-EL III CHNS Analyser.

III. RESULTS AND DISCUSSION

A. *Crystal Growth*

Using the crystallisation method described in section 2.1, crystals of PbM were formed at the gel interface within one week. The growth process took four weeks for completion. Good quality single crystals suitable for single crystal XRD studies were grown in gel medium of pH 5.5 and density 1.04g/cc with 1M maleic acid and 0.5M lead nitrate.The characteristic shape of the crystal is shown in Fig. 1.

Fig. 1: Photo of grown PbM crystal.

B. *Crystal structure*

The single crystal XRD data of a well formed crystal were collected using Bruker AXS Kappa Apex2 CCD diffractometer with graphite monochromated Mo Kα (λ= 0.71073Å) radiation. SAINT/XPREP program is used for data reduction [4]. The program SIR92 was used for solving the crystal structure and the refinement was carried out by Full-Matrix least squares on F2 using SHELXL-97 [5, 6]. Anisotropic thermal parameters were applied to refine all the nonhydrogen atoms. The hydrogen atoms were located from the difference Fourier maps and refined isotropically. Molecular graphics were constructed using the IUCR software Mercury (Version 3).

A report on the structure of lead maleate grown at higher temperature is available [2].The report on the growth of title complex at room temperature is not available so far. Good quality crystals of lead maleate are grown by gel method for the first time. The PbM crystals thus grown by gel method belongs to the space group P21/C with unit cell parameters a= 9.8795(3) Å, b=6.9537(3) Å, c= 8.2616(4) Å, β= 111.121(2)◦. The crystallographic data and processing parameters, fractional atomic co-ordinates, bond lengths and bond angles are comparable with the values as reported by Bonhomme et al. [2]. Asymmetric unit consist of a lead atom and a maleate ligand as shown in fig.2. The co-ordination environment of PbM is shown in fig. 3. Each independent lead atom is 7 co-ordinated to the oxygen atoms of maleic acid units.Each maleate anion is bonded to four lead atoms. Here, O1, O3, O4 are linked to two lead atoms, while O2 is bonded to one. The ligand thus show bidendate and unidendate mode of co-ordination with the metal atom. The Pb-O distance ranges from 2.413Å to 2.839Å, which is comparable with the previously reported values. The shortest distance between the two lead ions is 3.87Å. The O-C-O angle of maleate anion ranges from 121.32◦ to 122.05◦. The C1-C2 and C3-C4 bond lengths are equal to 1.472Å and 1.492Å respectively which is comparable with the reported values. The C=C bond length is equal to 1.308Å which is less by 0.032Å from the reported value. The absolute value of the main torsion angle of carbon skeleton of the maleate ligand is 3.2(15)◦. The intra molecular hydrogen bond normally found in the maleic acid molecule is not found in the present case [7]. But the Oxygen atom O2 forms two weak hydrogen bonds with the adjacent H2 and H3 at 2.65Å and 2.56Å.This weak interlayer hydrogen bonding stabilises the crystal structure and forms the 2D polymeric structure of PbM. Fig.4 shows the packing of PbM along the b axis.

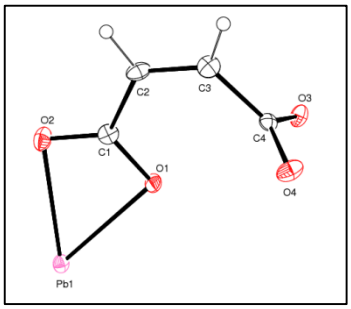

Fig 2. Asymmetric unit of PbM

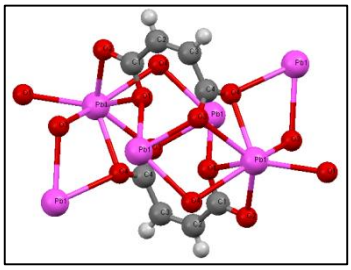

Fig 3. Co-ordination environment of PbM

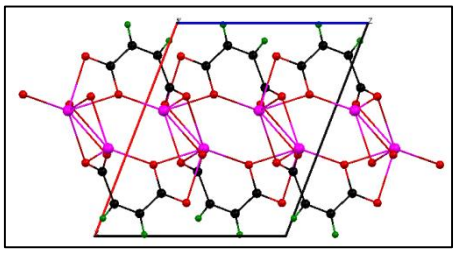

Fig. 4: View of packing along b axis in PbM

C. *FT-IR spectral studies*

The co-ordination of the metal ion with the organic linker is reflected as the shift in the vibrational frequency of the complex. The FTIR spectrum of PbM is shown in fig.5.The absence of broad band around 3400cm-1 confirms the absence of water of ligation in the structure of PbM [8]. The bands of protonated carboxylic groups are usually expected in the range 1685-1715cm-1. These bands are absent in the PbM spectrum indicating the complete deprotonation of this group which is supported by SXRD. The band at 1642cm-1is assigned to the asymmetric stretch

while the band at 1406 cm-1and 1535cm-1is assigned to the symmetric stretch of the carboxylate group [9].Thus the Δν value of 236cm-1and 129cm-1corresponds to the unidendate andbidendate mode of co-ordination of the ligand with the metal, which is evident from the SXRD data.The band at 1530cm-1due to νC=C in the ligand spectrum shifts down to 1496 cm-1in the complex spectrum. This may be due to the C-H…O interaction in PbM. The band at 989cm-1in the ligand spectrum due to the C-H out of plane bending vibration shifts down to 973cm-1, which may be due to the presence of intermolecular hydrogen bonds. Pb-O stretching is identified by the band at 461cm-1[10].

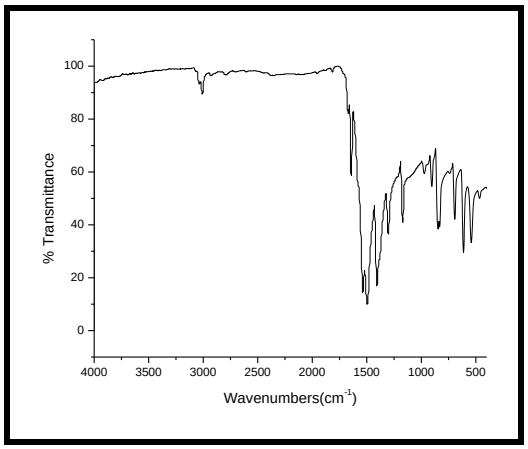

Fig5. FTIR spectrum of PbM

D. Elemental analysis

The elemental composition of PbM crystals was determined both theoretically and experimentally. Both the values are in agreement with each other and the molecular formula is derived as $PbC_2H_2(CO_2)_2$.

Experimental: C- 14.81%, H- 0.69%; Calculated: C- 14.95%, H- 0.63%.

E. Thermal analysis:

TGA/DTA data provides the details regarding the thermal stability of the complex. An amount of 15.5 mg is taken for the analysis.The results of TGA and DTA studies are given in Fig.6. PbM is thermally stable upto 250◦C. This confirms the absence of lattice water and co-ordinated water molecules. This is followed by an endothermic peak at 337◦C which indicates the elimination of organic ligand to form metal oxide, PbO and elemental carbon residue with a weight loss of 26 %(cal: 26.89%). Weight of the final residue PbO + C (74%) observed from thermal studies is found to be in agreement with the calculated residual weight of 73.11% [11].

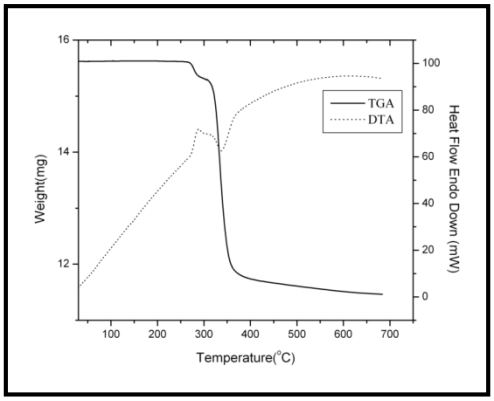

Fig6: TGA/DTA of PbM

F. UV- Vis spectral studies

To know the suitability of the material for optical applications, UV- Visible absorbance spectrum of PbM crystals was carried out between 200 nm and 1200nm. Fig. 7 shows the absorbance spectrum of the complex. The crystal is found to be transparent in the entire visible region which enables it to be a good candidate for optoelectronic application [12]. A graph is drawn between photon energy hν versus (αhν)2, where α is the absorption coefficient,as shown in fig.8 and the bandgap is estimated as 4.3eV. Using the results of single crystal XRD and UV-Vis data, Plasma energy, fermienergy and polarisability of PbM is calculated as 21.4 eV, 17.5 eV and 1.5E-23cm^3 respectively[13].

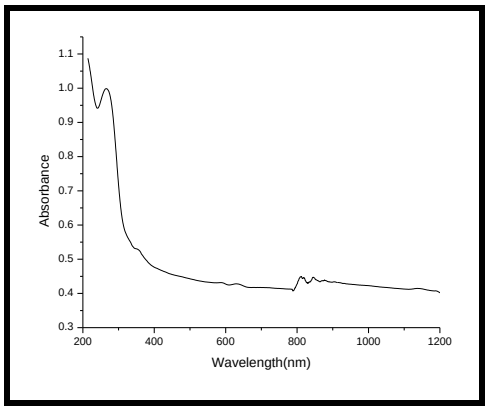

Fig 7:Absorbance spectrum of PbM

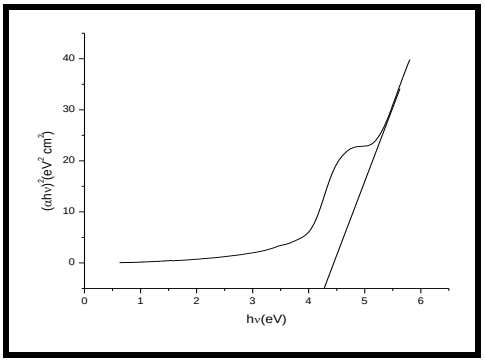

Fig. 8: Plot of alpha energy versus photon energy

IV. CONCLUSIONS

Single crystals of lead maleate are grown successfully by conventional gel method for the first time. Good quality single crystals belonging to monoclinic system, P21/C space group are grown from the gel medium of pH 5.5 and density 1.04g/cc. The crystal structure was same as that of the reported one. Thus the crystal structure is not affected by the change in the method of crystallisation. The 2D polymeric crystal structure is stabilised by the intermolecular hydrogen bonding as revealed by the single crystal XRD data. The FTIRspectral analysis confirms the presence of various functional groups in the grown crystals. The elemental analysis is consistent with thechemical formula $PbC_2H_2(CO_2)_2$.The thermal stability of the complex is provided by the TGA/ DTA. Wide transparency of PbM in the entire visible range makes it a suitable candidate for optoelectronic application. The porosity of the complex offers the potential for gas adsorption and storage.

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