

Thermal and infrared studies of calcium malate crystals grown in diffusion limited medium

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Single crystals of the title compound $\text{Ca}(\text{C}_4\text{H}_5\text{O}_5)_2 \cdot 10\text{H}_2\text{O}$ are grown in silica gel using controlled chemical reaction method. Multifaceted single crystals of size up to $8 \times 4 \times 2 \text{ mm}^3$ are obtained. Powder X-Ray Diffraction (XRD) pattern of the grown crystal and the Fourier Transform Infra-Red (FTIR) spectrum in the range $400\text{--}4000 \text{ cm}^{-1}$ are recorded. The vibrational bands corresponding to different functional groups are assigned. Thermal decomposition stages observed in the Thermo-gravimetric (TG) and Differential Thermal Analysis (DTA) studies are discussed. A six-stage thermal decomposition scheme is proposed for the compound.

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1 Introduction

Metal complexes of various carboxylic acids have attracted the specific attention of many researchers for long time due to their overwhelming practical applications in science and technology. Monocarboxylates, such as formates and acetates of many metals are examples of this group, which have been grown and characterized widely by different methods [1-8]. The growth and characterization of metal complexes of dicarboxylate crystals like oxalates [9-14], malonates [15-16], maleates [17-20] and substituted acids like tartrates and lactates [21-24] caught major attention due to their optical and ferroelectric properties. Like oxalates, malates also form polyhydrated salts with calcium. Though some studies report the precipitation of calcium malate [25-29], no work has been cited in the literature regarding the growth of single crystals of the same. In this report, we present the crystallization of calcium malate by the diffusion-controlled process in silica gel medium and its spectroscopic as well as thermal characterization.

2 Experimental

Single crystals of calcium malate were prepared by the ionic diffusion technique in hydro-silica gel. Analar grade malic acid, calcium chloride (CaCl_2) and sodium meta silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) were the chemical components used in the experiment. Silica gel was prepared from its aqueous solution after mixing with malic acid [30]. The strength of the acid and its volume were adjusted to obtain the desired pH. Borosil tubes of inner diameter 2 cm and length and 20 cm were used as the crystallization vessels. Sodium meta silicate solution, impregnated with malate ions was taken inside the tubes for gelation. Surface contamination by external impurities was prevented by covering the tubes by paraffin-coated lids. The experiment was performed in ambient atmosphere where the day-night temperature variation was below $\pm 5\text{K}$. The outer reacting component, calcium chloride solution was poured over, taking adequate care not to distort the delicate gel meniscus. A series of experiments were conducted at various gel densities and pH values to study the growth kinetics. Concentrations of inner and outer solutions were also varied to study the growth conditions. Crystallization process was slow and tiny crystals were observed at the gel-solution interface in about ten days. Crystals attained their maximum size in 25-30 days. Crystals having well-developed faces were carefully separated from the medium, and spectroscopic as well as thermal investigations were made on them.

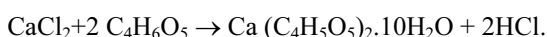
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Well-developed crystals devoid of inclusions were ground to fine powder and diffraction pattern was recorded. The JEOL-JDX 8030 X-Ray Diffractometer was used for recording the spectrum with wavelength 1.5418 Å. Characterization was done using the Fourier Transform Infra-red (FTIR) spectrum of the sample recorded on a Thermo Nicoline spectrophotometer in the range 400 – 4000 cm⁻¹ using KBr pellet method. The resolution of the instrument was 4 cm⁻¹. Also, the thermal behavior of the crystals was studied by TG-DTA technique carried out using STA 1500 Simultaneous Thermal Analysis System (PL Thermal Sciences Division, UK). For this the sample was heated from room temperature to 900 °C at a rate of 10 K/minute in nitrogen atmosphere.

3 Results and discussion

3.1 Crystal formation

The optimum condition for growing defect free crystals of calcium malate are identified as pH 3 in a gel of density 1.06 gm/cc. Concentrations of the inner and outer reactants respectively were 1 M and 0.5 M. The gelation time was one week and growth was initiated in ten days. The possible chemical reaction involved in the precipitation of the compound and subsequent formation of crystals is:



Crystals of maximum size 8 x 4 x 2 mm³ were yielded from the experiment. They were prismatic and colorless. These crystals, which appeared to be transparent inside the gel, become translucent when exposed to atmosphere.

3.2 Powder XRD studies

Powder XRD spectrum of the sample is shown in fig.1. Relative intensities and corresponding d- values of the peaks are found out which are given along with the 2θ values in table 1.

Table 1 Observed 2θ, d-spacings and relative intensities obtained from XRD studies.

2θ	d(Å)	I/I ₀
13.700	6.458	41
16.200	5.467	100
26.300	3.386	8
29.400	3.035	10
32.600	2.744	9
35.600	2.520	6
46.600	1.947	6
55.600	1.652	3

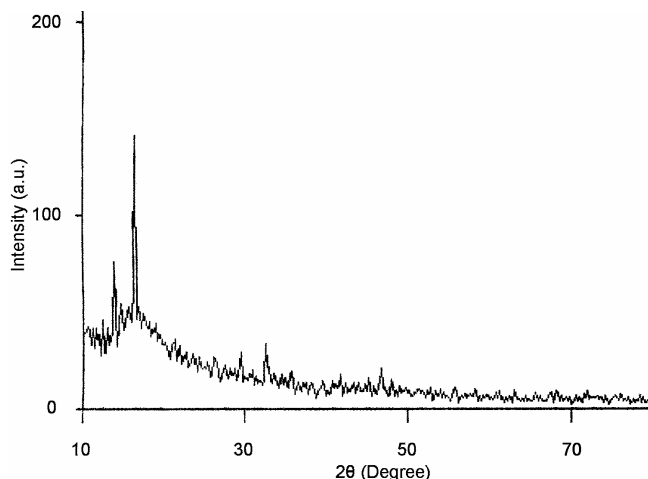


Fig. 1 XRD pattern of calcium malate crystals.

3.3 FTIR studies

The recorded FTIR spectrum of the crystal is given in fig. 2. From the spectrum, information regarding the vibrational modes of different functional groups present in the compound can be extracted. Absorption frequencies observed are compared with those data available in literature [31-39]. Vibrations corresponding to different functional groups confirm the structure of the title compound. Bands assigned to various vibrations of the crystal are listed in table 2.

The strong peak around 3191 cm⁻¹ corresponds to the symmetric stretching of -OH group. Broad peak centered around 2650 cm⁻¹ represents the stretching of -CH group in the compound. Bending of the H-O-H group in the crystal is confirmed by the strong peak at 1724.10 cm⁻¹. Antisymmetric and symmetric stretching of the carboxylate group occurs at wavenumbers 1590.68 cm⁻¹ and 1400.92 cm⁻¹ respectively. Bands at

1452.28, 1299.39 and 1266.33 cm^{-1} are ascribed to the deforming modes of the methylene group. The strong band at 1093.70 cm^{-1} is attributed to the vibrations of the -CH group. Rocking modes of methylene group occurs at 994.74 cm^{-1} . The C-C stretching band is revealed at 912.49 cm^{-1} . Medium bands at 875.50 and 808.58 cm^{-1} are attributed to the rocking and wagging modes of water molecules. Librational bands of water are found appearing at 586.26 cm^{-1} , 519.99 cm^{-1} and 413.26 cm^{-1} . Metal oxygen stretching in the crystal is represented by the medium band centered at 677.17 cm^{-1} .

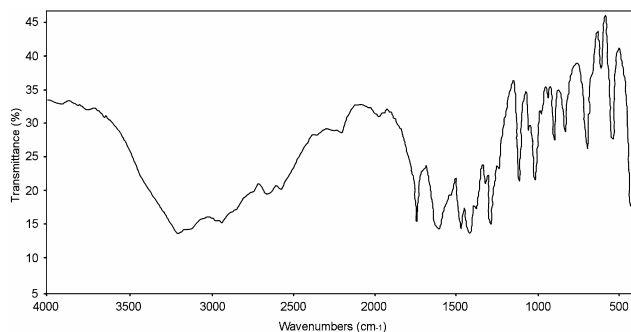


Fig. 2 FTIR spectrum of calcium malate crystals.

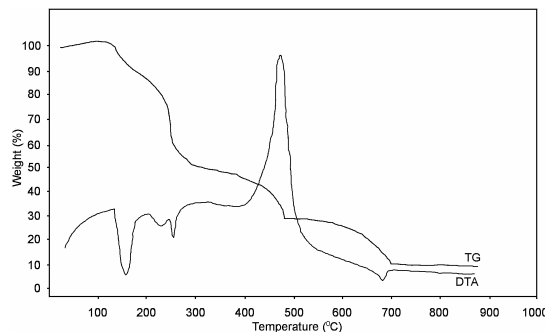


Fig. 3 Thermogram showing TG and DTA curves of the crystals.

Table 2 Spectral assignments of the IR peaks.

Wave number (cm^{-1})	Assignment
3191.56	ν_s O-H
2650.37	ν CH
1724.10	δ H-OH
1590.68	ν_{as} COO
1452.28	δ CH ₂
1400.92	ν_s COO
1299.39	δ CH ₂
1266.33	δ CH ₂
1093.70	π CH
994.74	ρ_r CH ₂
912.49	ν CC
875.50	ρ_r H ₂ O
808.58	ρ_w H ₂ O
677.17	ν M-O
586.26	ρ_w H ₂ O
519.99	ρ_t H ₂ O
413.25	ρ H ₂ O

3.4 Thermal properties

The TG and DTA curves for the sample are shown in fig. 3. Thermal decomposition and stability of the sample were analyzed with the help of these curves. It is observed that all the transformations are associated with some mass loss. It suggests that there is no structural change independent of mass change in the compound. It is evident from the TG curve that the compound is thermally stable up to 120 °C. Initial stages in the decomposition process are due to the liberation of hydrated water. Two molecules of water are eliminated in the temperature range 120-160 °C. The dehydration process gets completed at 250 °C, leading to anhydrous calcium dihydrogen malate [$\text{Ca}(\text{C}_4\text{H}_5\text{O}_5)_2$]. The forthcoming stage of decomposition taking place in the temperature range 250-300 °C, results in the formation of $\text{Ca}(\text{C}_2\text{HO}_4)_2$ and elementary carbon. They are further transformed into calcium oxalate at 480 °C. Carbon monoxide and hydrogen molecules are eliminated in both the steps. Further heating up to 630 °C results in the conversion of oxalate group to carbonate along with the

elimination of carbon dioxide. This calcium carbonate is reduced to calcium oxide in the final stage of decomposition, which is complete at 700 °C. Further decomposition of the compound is not observed on heating up to 900 °C. Various stages of thermal decomposition and corresponding mass losses are tabulated in table 3. The observed percentage of mass loss in each stage is in fair agreement with the calculated one.

All the peaks in the DTA curve give additional support to the TG results. The broader endotherms below 250 °C correspond to the dehydration process. The exothermic peak observed near 490 °C is indicative of the transformation of calcium oxalate into calcium carbonate with the liberation of carbondioxide. The endothermic peak near 700 °C shows the decomposition of calcium carbonate to calcium oxide.

Table 3 The decomposition process of $\text{Ca}(\text{C}_4\text{H}_5\text{O}_5)_2 \cdot 10\text{H}_2\text{O}$.

Stage	Decomposition temperature (°C)	Product after decomposition	Molecules evolved	Observed mass loss (%)	Calculated mass loss (%)
I	120-160	$\text{Ca}(\text{C}_4\text{H}_5\text{O}_5)_2 \cdot 8\text{H}_2\text{O}$	2 H ₂ O	7.0	7.408
II	170-250	$\text{Ca}(\text{C}_4\text{H}_5\text{O}_5)_2$	8 H ₂ O	28.5	29.631
III	250-300	$\text{Ca}(\text{C}_2\text{H}_4\text{O}_4)_2 + 2\text{C}$	2CO+4H ₂	13	13.175
IV	300-480	$\text{Ca}(\text{C}_2\text{O}_4)$	4CO+H ₂	23.2	23.449
V	490-630	CaCO_3	CO ₂	8.8	9.048
VI	650-700	CaO	CO ₂	8.7	9.048

4 Conclusions

Diffusion of supernatant calcium chloride into the silica gel impregnated with malic acid results in the formation of calcium malate crystals. The powder XRD pattern reveals the strong crystalline nature of the sample. Single crystal analysis for the exact determination of the structure is in progress. Results of IR and thermal studies establish the compound to be hydrated having the stoichiometry $\text{Ca}(\text{C}_4\text{H}_5\text{O}_5)_2 \cdot 10\text{H}_2\text{O}$. Presence of different functional groups and bonds are also revealed by the IR spectrum. Thermal behavior suggests that the material is stable up to 120 °C. Passing through various intermediate stages it ultimately gets reduced to calcium oxide at 700 °C. Thermograms show that all transformations are associated with mass change, which rules out the possibility of any change in the crystal structure of the original compound.

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