

## Structural, Spectroscopic, Magnetic and Thermal Studies of Gel-Grown Copper Levo-Tartrate and Copper Dextro-Tartrate Crystals

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**Abstract:** Metal tartrate compounds find various applications. In the present study, the effect of optically sensitive levo-tartaric acid and dextro-tartaric acid on growth and various physical properties of copper (II) levo-tartrate and copper (II) dextro-tartrate crystals were investigated. The crystals were grown in silica-hydro-gel medium. The optimum condition was established at room temperature by various parameters such as pH of gel solution, gel solution specific gravity and concentration of reactants. Transparent, prismatic and blue colored single crystals were obtained. The crystals were characterized by powder XRD, FTIR, EPR, VSM and TGA. Copper levo-tartrate and copper dextro-tartrate exhibited small but remarkable difference in their properties. Copper levo-tartrate exhibited higher values of unit cell volume, orthorhombicity and magnetic susceptibility than copper dextro-tartrate crystals. However, copper dextro-tartrate gave higher values of dehydration temperature and  $g_{\perp}$  at liquid nitrogen temperature in X-band EPR spectra than copper levo-tartrate crystals. This has been discussed on the basis of their molecular structural configurations.

**Keywords:** Copper dextro-tartrate, copper levo-tartrate, EPR, FTIR, Powder XRD, silica gel, TGA, VSM.

### I. Introduction

Even though the gel growth is having certain limitations, it is a suitable method to grow crystals of materials which are sparingly soluble in water and which cannot be conveniently grown by vapor or melt growth techniques. Several metal tartrate crystals have been successfully grown by the gel method [1-6]. Copper tartrate finds several applications, such as temperature indication based on change in coloration on heating [7], in study of copper mediated oxidation of thiols in the regulation of the release of Luteinizing Hormone Releasing Hormone (LHRH) [8], in carbon fiber floret production as a catalyst [9] and in blood sugar determination by Folin method [10]. The effect of light on copper tartrate has been examined [11].

The growth of copper tartrate crystals was reported by several authors using the gel-growth method [12-14]. Also, several doped copper tartrate crystals were grown by the gel technique, for example, sodium modified [15], iron doped [16] and manganese [17] doped copper tartrate crystals.

Tartaric acid (2,3-dihydroxybutanedioic acid, 2,3-dihydroxy Succinic acid),  $C_4H_4O_6$ , is a dihydroxy dicarboxylic acid with two chiral centers. It exists as the dextro and levo rotatory acid, the meso- form (which is inactive owing to internal compensation), and the racemic mixture (which commonly is known as racemic acid). This enantiomer occurs in grapes as its acid potassium salt (cream of tartar). The dextro and levo rotatory tartaric acids as well as meso tartaric acid are shown in Fig. 1 in stereo-chemical configuration.

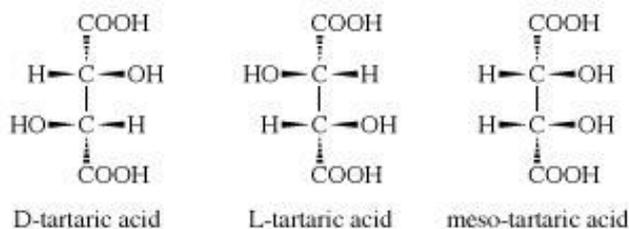
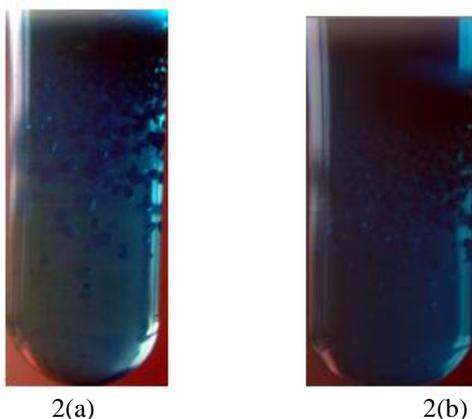


Figure 1

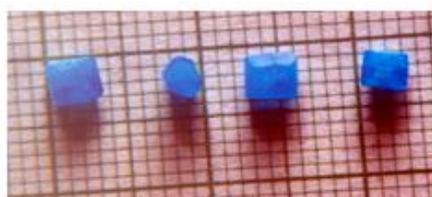
Looking at significant applications of copper tartrate and limited study carried out on stereo selective effects in the complex formation between the copper (II) ion and optically active and racemic tartrate [18-21], the present authors have hereby attempted to grow copper tartrate crystals using optically sensitive dextro-tartaric acid and levo-tartaric acid and study the effect of optically active tartaric acid on growth and crystalline properties using powder XRD, FTIR, EPR, VSM and TG analysis.

## II. Experimental

The crystallization apparatus employed for the present investigation consisted of glass test tubes of 25 mm diameter and 140 mm length. The AR grade chemicals were used to grow the crystals. One of the reactants, 1M dextro tartaric acid or 1M levo tartaric acid, was mixed with sodium metasilicate solution to prepare the gel in such a way that the pH of mixture was maintained in the range of 4.2 to 5.5. The specific gravity of the gel was varied between 1.02 to 1.07. After setting the gel, the supernatant solution of CuSO<sub>4</sub> having concentrations of 0.5 M and 1M were gently poured without disturbing the gel surfaces. The growth of crystals was completed within the period of one month. The single crystals were blue color, transparent and prismatic in nature. The best quality crystals were grown at 4 pH, specific gravity of 1.04 and with CuSO<sub>4</sub> solution of 1M concentration. Fig. 2 shows the growth of copper (II) levo and dextro tartrate crystals in gel and Fig. 3 shows the harvested crystals.



**Figure 2:** The growth of copper levo-tartrate crystals (a) and copper dextro-tartrate crystals (b) in gel medium in test tubes



**Figure 3:** Harvested copper (II) levo and dextro tartrate crystals

The following reaction is expected to take place in the formation of copper levo-tartrate/copper dextro-tartrate crystals.



The amount of H<sub>2</sub>SO<sub>4</sub> produced is very less in comparison with the nutrients being supplied to the growing crystals and hence no major limitation is imposed [16,22,23].

The grown crystals were characterized by different techniques. The powder XRD patterns were recorded on PHILIPS X'PERT MPD System. The FTIR spectra were recorded on NICOLET MAGMA IR 550 Series II FTIR Spectrometer, in the range from 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. The magnetic susceptibility of the crystals was measured using EG and PARC-155 Vibrating Sample Magnetometer at room temperature with different applied magnetic fields at R. S. I. C., IIT, Madras, Chennai. The EPR study was carried out in X-band (8.5 to 9.5 GHz) and Q-band (35.5 GHz) at room temperature as well as at liquid nitrogen by using VARIAN E112 ESR Spectrometer at R.S. I.C., IIT, Madras, Chennai. Thermo-gravimetric analysis was carried out from room temperature to 950°C at a heating rate of 15 °C/min in an atmosphere of air using α-Al<sub>2</sub>O<sub>3</sub> as standard reference using Perkin Elmer, Pyris – 1 TGA set up.

## III. Results And Discussion

### 3.1 Powder XRD

Bridle and Lomer [12] reported the growth of copper tartrate crystals in silica gel and obtained its unit cell dimensions as:  $a = 8.42 \text{ \AA}$ ,  $b = 12.33 \text{ \AA}$ ,  $c = 8.82 \text{ \AA}$  and  $\alpha = 97^\circ 21'$ ,  $\beta = 80^\circ 43'$ ,  $\gamma = 115^\circ 42'$ . The structure of copper levo-tartrate reported by Soylyu [24] is  $a = 8.374(4) \text{ \AA}$ ,  $b = 12.849(7) \text{ \AA}$ ,  $c = 8.758(6) \text{ \AA}$ .



### 3.2 TGA

Fig. (5a) and Fig. (5b) show the thermo-grams of copper levo-tartrate and copper dextro-tartrate, respectively.

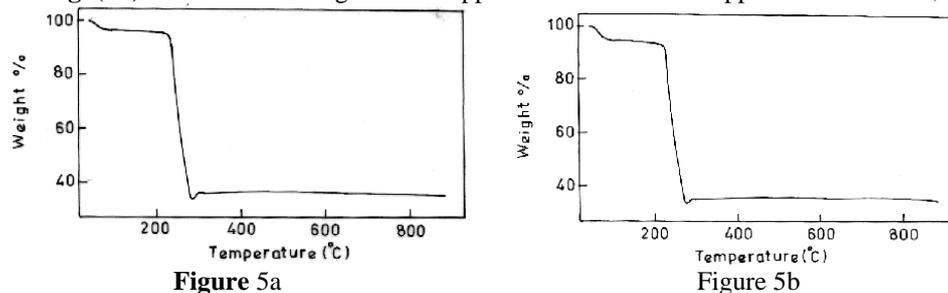


Figure 5: TG curves of (a) copper levo-tartrate and (b) copper dextro-tartrate crystals

One can see from Fig. 5a that the hydrated copper levo-tartrate crystals dehydrate into anhydrous form at 85°C, which is followed by a rapid decomposition into CuO at 295°C. Fig. 5b shows the decomposition process of copper dextro-tartrate crystals. Hydrated copper dextro-tartrate crystals become anhydrous at 105°C, thereafter, a sharp decomposition takes place and CuO is formed at 290°C. Both of these thermo-grams are similar in nature and show nearly the same temperature values, however, copper dextro-tartrate dehydrate at higher temperature. From these two figures, it can be seen that a small dip is occurring near by 280°C and, thereafter, the stable state is taking place, which may be due to anhydrous copper tartrate first decomposes into Cu + 1/2O and subsequently picks up oxygen from air and becomes CuO. Both the crystals are found to be having 0.5 water molecules associated with them. It has been observed that copper levo-tartrate and copper dextro-tartrate crystals are thermally sensitive on exposure to air and on slight heating they lose their coloration and become pale blue powder like samples.

Table 2 indicates the decomposition process of copper levo-tartrate and copper dextro-tartrate crystals with theoretically calculated and experimentally observed weight % results.

Table 2: Thermal decomposition results from TG curves

Sample	Temperature (°C)	Decomposition of crystals	Theoretical weight (%)	Observed weight (%)
copper levo-tartrate	Room temp	CuC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> .0.5H <sub>2</sub> O	100	100
	85	CuC <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	95.9	96.50
	295	CuO	36.05	36.00
copper dextro-tartrate	Room temp	CuC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> .0.5H <sub>2</sub> O	100	100
	105	CuC <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	95.9	94.50
	290	CuO	36.05	35.00

### 3.3 VSM

Magnetic properties of a variety of materials have been investigated. Raina [25] studied the magnetic properties of neodymium tartrate by using Gouy's method. Magnetic properties of copper chloride hydroxide hydrate Cu<sub>3</sub>Cl<sub>4</sub>(OH)<sub>2</sub>·2H<sub>2</sub>O was investigation by Asaf et al. [26]. This has shown interesting behaviour, a weak ferromagnetic signal at T<sub>N</sub> = 17.5 K has been observed in the FC branch of d.c. magnetic susceptibility. Joshi et al. [22] reported magnetic susceptibility of iron-manganese-cobalt ternary levo-tartrate crystals by using VSM. Jethva [27] has reported magnetic susceptibility measurements of mixed iron-lead levo-tartrate crystals by using VSM and found a paramagnetic nature. However, Binitha and Pradyamnan [14] reported diamagnetic nature of copper tartrate.

In the present case the magnetic study was carried out by using vibrating sample magnetometer. Table 3 indicates the variation in magnetic moment and bulk susceptibility with different applied magnetic fields for copper levo-tartrate and copper dextro-tartrate crystals at room temperature.

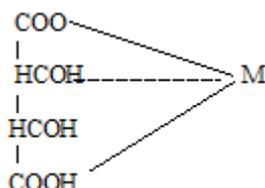
Table 3: Magnetic moment and bulk susceptibility values of copper levo and dextro tartrate crystals

Sample	Applied magnetic field (Tesla)	Magnetic moment (EMU) × 10 <sup>-1</sup>	Bulk susceptibility (A.m <sup>2</sup> /kg.T) × 10 <sup>-5</sup>
Copper levo-tartrate	0.4	0.004	0.3571
	0.6	0.010	0.5952
	0.8	0.009	0.4018
	1.0	0.010	0.3571
Copper dextro-tartrate	0.4	0.001	0.1078
	0.6	0.002	0.1437
	0.8	0.001	0.0539
	1.0	0.003	0.1293

It can be seen that both samples are paramagnetic in nature. From Table 3, it can be easily seen that the variation of magnetic moment and bulk susceptibility with applied magnetic field is not systematic. The bulk susceptibility values of copper dextro-tartrate are lower than copper levo-tartrate crystals, which may be due to different types of optically sensitive tartaric acids present in the samples.

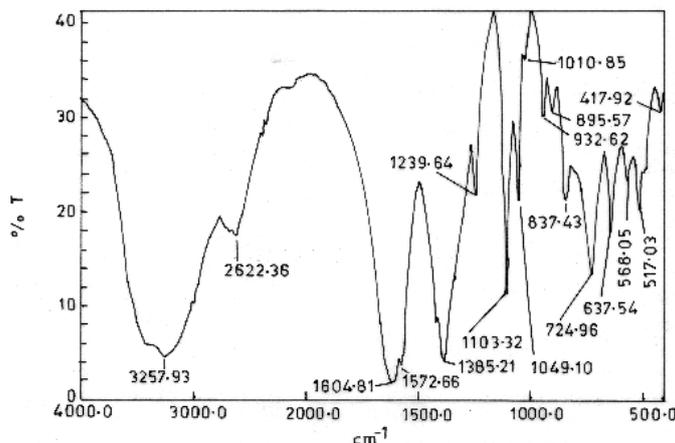
### 3.4 FTIR

Shevehoko [28] studied the IR spectra of both normal and partially deuterated compounds of some tartrates and found absorptions at  $600\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$  due to COO group in metal tartrates. The formula of metal tartrate was suggested as follows.

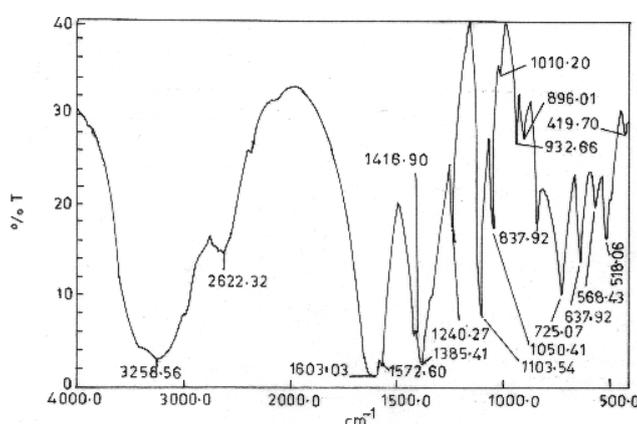


Moreover, Kirschner and Kiesling [29] studied the infrared spectrum of Cu (II) tartrates tri-hydrate. They found that tartrate was coordinated to Cu (II) through hydroxyl and 2-carboxylate groups and proposed the octahedral structure with three water molecules.

Fig. (6a) and Fig. (6b) indicate FTIR spectra of copper levo-tartrate and copper dextro-tartrate crystals, respectively.



**Figure 6(a):** FTIR spectrum of copper levo-tartrate crystals



**Figure 6(b):** FTIR spectrum of copper dextro-tartrate crystals

Both spectra confirm the presence of O-H and C-H functional groups and metal oxygen vibrations. Assignments for different absorption bands in FTIR spectra for copper levo-tartrate crystals and copper dextro-tartrate crystals are given in Table 4. One can notice that both spectra are nearly the same and no effect of optically sensitive levo-tartaric acid and dextro-tartaric acid on the growth of crystal is observed from FTIR spectral studies. As the FTIR spectral study does not through much light, the EPR spectral study is further carried out.

**Table 4:** Assignments for FTIR spectra

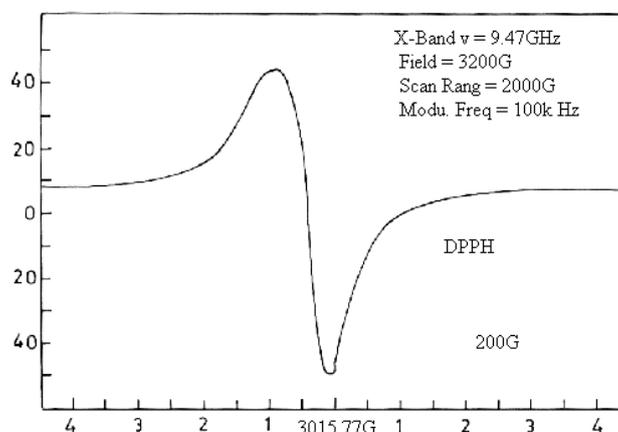
Assignments	Wave number (cm <sup>-1</sup> )	
	copper levo-tartrate crystals	copper dextro-tartrate crystals
O-H stretching	3257	3258
C=O stretching	1604 and 1572	1603 and 1572
C-O stretching vibration	1385 and 1239	1385 and 1240
C-H stretching vibration	1103	1103
O-H stretching out of plane vibration	1049	1050
Metal oxygen bond (Cu-O stretching)	724, 637 and 517	725, 637 and 518

### 3.5 EPR

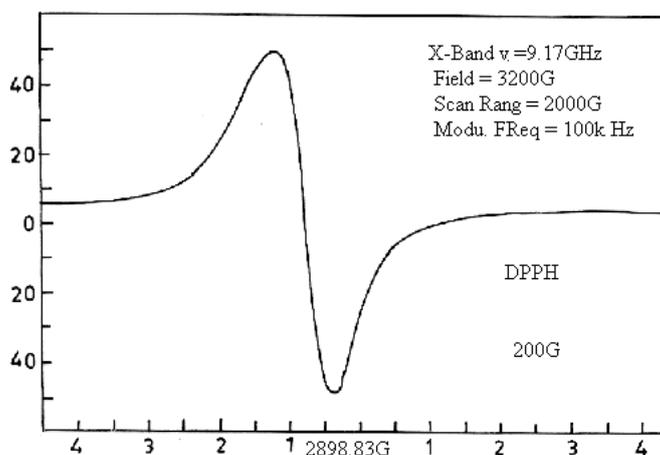
Ablov et al. [30] have carried out EPR and magnetic susceptibility studies of the copper compound of *d*-tartaric acid. The EPR spectra are examined at 1:1 complexes of copper with mesoactive and racemic tartaric acid in acidic (pH about 4) and basic (pH about 11) solutions at 80°K and 300°K by Dennis [31]. Chasten and Belford [19] reported the EPR parameters as  $g_{\parallel} = 2.224$ ,  $g_{\perp} = 2.139$  and  $g_{\perp} = 2.08$  and  $A = 0.0082 \text{ cm}^{-1}$  for  $\text{Cu}_2(\text{dl-tartrate})_2^{-4}$  species in solution.

In the present investigation, copper dextro-tartrate and copper levo-tartrate crystals in powder form have been characterized by EPR spectroscopic studies in the X-band as well as the Q-band regions at room temperature. However, in the X-band region, the samples have also been characterized at liquid nitrogen temperatures.

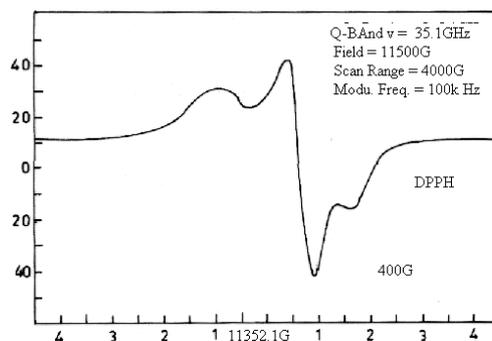
Fig. (7a) is EPR spectrum of copper dextro-tartrate at room temperature, which is more or less isotropic type behavior. Fig. (7b) is liquid nitrogen temperature EPR spectrum of copper dextro-tartrate in X-band, which shows the similar nature. The  $g_{\perp}$  values have been calculated and found to be 2.3038 and 2.4018 for room temperature and liquid nitrogen temperature, respectively, in X-band. However, the Q-band EPR spectrum is resolved further. The value of  $g_{\perp}$  for the Q-band EPR spectrum is found to be 2.1607. Fig. (7c) shows this spectrum.



**Figure 7(a):** X-band EPR spectrum of copper dextro tartrate at room temperature

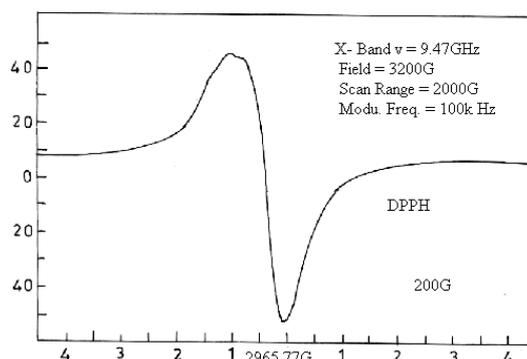


**Figure 7b:** X-band EPR spectrum of copper dextro tartrate at liquid nitrogen temperature

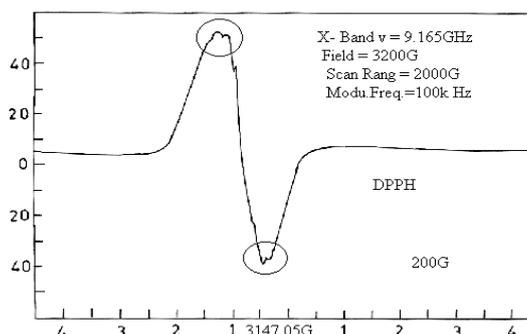


**Figure 7c:** Q-band EPR spectrum of copper dextro tartrate at room temperature

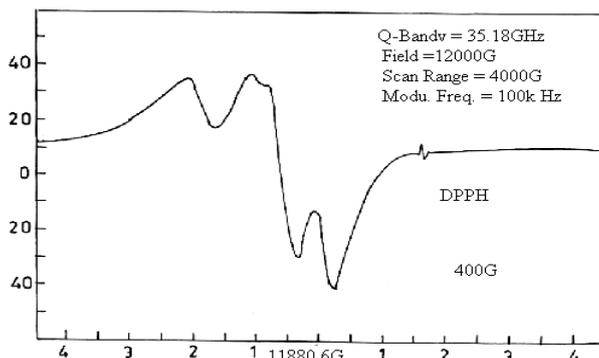
The EPR spectrum of copper levo-tartrate crystals recorded in the X-band at room temperature shows asymmetric absorption peak as shown in Fig. 8a. On cooling the sample at liquid nitrogen temperature shows minor hyperfine structure as indicated in Fig. 8b with circles. This may be due to change in the symmetry of environment of Cu(II) at liquid nitrogen temperature. Taking the EPR spectrum at room temperature in the Q-band region shows further in two distinct asymmetric peaks, which is shown in Fig. 8c.



**Figure 8a:** X-band EPR spectrum of copper levo tartrate at room temperature



**Figure 8b:** X-band EPR spectrum of copper levo tartrate at liquid nitrogen temperature



**Figure 8c:** Q-band EPR spectrum of copper levo tartrate at room temperature

The value of  $g_{\perp}$  is found to be 2.1622 for the Q-band, whereas, the value of  $g_{\perp}$  are 2.3438 and 2.1914 for room temperature and liquid nitrogen temperature X-band spectra, respectively. The Q-band spectra of copper dextro-tartrate and copper levo-tartrate both are asymmetric but having a marked difference. This may be due to different structure of dextro-tartrate and levo-tartrate radicals with copper ion. The values of  $g_{\perp}$ -factor are displayed in Table 5.

**Table 5:** Values of  $g_{\perp}$  factor for different EPR bands

Sample	EPR band	Temperature	$g_{\perp}$ value
copper dextro-tartrate crystals	Q-band	Room temperature	2.1607
	X-band	Room temperature	2.3038
	X-band	Liquid nitrogen temperature	2.4018
copper levo-tartrate crystals	Q-band	Room temperature	2.1622
	X-band	Room temperature	2.3438
	X-band	Liquid nitrogen temperature	2.1914

The anisotropic spectra of copper (II) complexes in the Q-band frequencies are well discussed by Drago [32]. In the present investigation, the hyperfine splitting was not observed in EPR spectra because pure powdered samples were used instead of doping in diamagnetic matrix or single crystals or dissolving in a suitable solution. Also, the symmetry of complex in solid state is expected to be affecting this. Very few complexes in the solid state have regular symmetry and classification into octahedral, tetrahedral, square planer etc., is only appropriate. In EPR investigations, it is convenient to classify the complex according to the nearest regular symmetry group and then to improve the description by introducing an appropriate distortion. As a result of this distortion, a degeneracy of d-orbital is further removed. Moreover, the inner symmetry of two carbons in tartrate radicals are different and, therefore, may be influencing the hyperfine splitting in the Q-band at liquid nitrogen temperature for both copper dextro-tartrate and copper levo-tartrate.

The properties of a particular ion in a particular environment are reflected in g-factors, nuclear hyperfine splitting, relaxation times, etc. The interpretation of measured g-factor hyperfine splitting and line width, conversely, will enable to build a picture of the orbital environment in constructing the ground state of the paramagnetic ion in its crystalline environment.

Earlier, Suthar and Joshi [33] studied EPR spectra of  $Mn^{+2}$  doped calcium levo-tartrate tetra-hydrate crystals and observed hyperfine splitting representing two large intensity and low intensity groups representing two in-equivalent  $Mn^{+2}$  centres.

Further, one can notice that the values of  $g_{\perp}$ -factor are comparatively higher in copper levo-tartrate in the Q-band and the X-band at room temperatures than in the case of copper dextro-tartrate. However, the value of  $g_{\perp}$ -factor for copper levo-tartrate at liquid nitrogen temperature is significantly less than that of the copper dextro-tartrate at liquid nitrogen temperature. This also indicates that some type of change in the environment symmetry of Cu (II) is occurring at liquid nitrogen temperature due to presence of levo-tartrate and dextro-tartrate radicals. This requires further investigations.

The difference in magnetic and EPR behavior of copper dextro-tartrate and copper levo-tartrate and also small but marked difference in other characterization can be explained on the basis of molecular structure and the complexes formed. Johansson [21] reported in detail different complex formation in aqueous solution between copper (II) ion and tartaric acid in the +, - and racemic forms in various pH ranges, i.e.,  $pH > 4$  and  $pH < 4$ . The occurrence of tartrate bridged bi-nuclear structure is well established in many crystal structures of metal tartrate [34-36]. In the assessment of conformation angles and strain induced in the central carbon-carbon bond of the tartrate ions in the tartrate bridged bi-nuclear complex, Tapscott [37] has suggested that the tetragonal coordination geometry with a planer arrangement of chelate ring is most favorable for rac-tartaric acid complex. It has been suggested [21] that tartrate bridged bi-nuclear complex may offer different geometries under different conditions as: (a) tetragonal geometry (rac-complex), (b) trigonal pyramid geometry (+ + - complex) and (c) octahedral geometry (+ + - complex).

It has been shown that the ESR spectra of copper (II) + - tartrate and copper (II) rac-tartrate solutions do not differ [19]. However, from the EPR and magnetic susceptibility measurements on powdered samples, Ablov et al [30] have proposed a polymeric chain model for copper d-tartrate dihydrate and each copper ion being coordinated with two halves of two different tartrate ions. Moreover, Prout et al [36] have proposed perfect octahedral geometry in dimeric copper tartrate unit in crystal structure of  $Cu(II) + - C_4H_4O_6 \cdot 3H_2O$ , but the geometries of the concerned complex in solution may have different form.

The clear difference in the values of  $g_{\perp}$  at liquid nitrogen temperature in X-band region of EPR spectra, as per our hypothesis is due to the difference in the nature of two halves of d-tartaric acid and L-tartaric acid ions coordinating each copper ions in a lattice. This difference may be high lighten in the X-band EPR spectra of liquid nitrogen temperature.

Basically, copper and water exhibit diamagnetic nature, however, copper (II) ions are paramagnetic. The paramagnetic behavior of copper tartrate can be explained. Earlier, Kohout and Kratsmar-Smogrovic [38]

reported bi-nuclear bridge structure of copper (II) acetate monohydrate, where two copper atoms are bonded by four acetate groups and the water molecules are linked to copper atoms in axial terminal positions. The close proximity of neighboring copper atoms, the Cu-Cu direct bonding likely to arise the lateral overlap of  $3d_{x^2-y^2}$  orbitals on each copper atom. Due to this bonding, the magnetic moment is depressed below the spin only value for one unpaired electron of  $3d^9$  configuration of Cu (II) ion. The magnetic susceptibilities of several copper (II) organic complexes were measured using Guoy's balance, including copper acetate [38] and found to be paramagnetic in nature near room temperatures, only a few compounds exhibited a diamagnetic nature at 77 K. In a fundamental work reported by Bleaney and Bowers [39] on anomalous paramagnetism of copper acetate, they argued that the isolated pairs of copper ions interacted strongly forces each pair forming a lower singlet state and on upper singlet state and result in paramagnetic nature.

The present authors propose a hypothesis that the bi-nuclear copper tartrate has different symmetry and strain environment on central carbon-carbon bond due to nature of legand in levo-tartrate and dextro-tartrate forms which may be responsible for different behavior in EPR spectra and the difference in magnetic susceptibilities values for copper dextro-tartrate and copper levo-tartrate crystals. However, further work is under progress for validation of this hypothesis. Both types tartrate crystals have the same number of water molecules associated with them. Notwithstanding, the difference in the thermal decomposition nature and unit cell parameters is small but quite clear to support this hypothesis.

#### IV. Conclusion

The copper levo-tartrate and dextro-tartrate crystals were grown in silica gel by using the copper sulphate as supernatant solution. The powder XRD suggested orthorhombic crystal structure of copper levo-tartrate and copper dextro-tartrate crystals. The values of unit cell parameters were appreciably matching closely with the values reported by Soylyu. The unit cell volume, orthorhombicity and X-ray crystal density values were slightly higher for copper levo-tartrate than copper dextro-tartrate crystals. From the TG curves, it was found that copper levo-tartrate and copper dextro-tartrate crystals were found to be thermally sensitive on exposure to air and on slight heating they lost their blue coloration and became pale blue powder like samples. During thermo-gravimetric analysis they first decomposed into anhydrous form and then sharply decomposed into  $Cu + 1/2O$ , thereafter, picking up oxygen from atmosphere and converted into  $CuO$ . Both the crystals were found to be having 0.5 water molecules associated with them. Copper levo-tartrate anhydrous crystals decomposed at slightly higher temperature than copper dextro-tartrate crystals. The results of vibrating sample magnetometry indicated that the copper levo-tartrate and copper dextro-tartrate crystals exhibited paramagnetic nature. The bulk magnetic susceptibility values of copper dextro-tartrate were lower than copper levo-tartrate crystals. The FTIR spectra of copper levo-tartrate and copper dextro-tartrate crystals were nearly the same and confirmed the presence of O-H, C=O and C-H functional groups, metal oxygen vibrations, however, they did not detect the effect of different optically sensitive tartaric acids in the samples. The EPR spectroscopic analysis suggested that the values of  $g_{\perp}$  factor were comparatively higher in the Q-band and the X-band at room temperature of copper levo tartrate crystals, than of these values for copper dextro tartrate crystal. However, the value of  $g_{\perp}$  factor for copper levo tartrate crystal was very less than that of the copper dextro tartrate crystal at liquid nitrogen temperature in X-band region of EPR spectrum. The spectra were anisotropic in the Q-band regions. In the present investigation the hyperfine splitting was not observed because of pure powdered samples were used instead of doping in diamagnetic matrix of single crystal. The difference in the properties can be explained on the basis of bi-nuclear nature of copper tartrate and different symmetry environment.

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