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ANTI-MICROBIAL ACTIVITY OF STRONTIUM TARTRATE COMPLEXES

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ABSTRACT:
A wide variety of mixed metal ligand complexes and their composites were studied by many researchers and discussed about their use in the medicinal chemistry, making of ferroelectric devices, piezoelectric transducers, magnetic sensors, and dielectric materials. The extensive literature survey carried out by us revealed that not much work has been done on studies related to use of various combinations of mixed metal-ligand complexes for antimicrobial applications. The present study deals with the synthesis, characterization, and evaluation of antimicrobial activity study of Strontium Tartrate complexes, which contain R=Sr (fixed metal ion) with R=Zn, Cu, Co, Mn (transition metal ions) bonded together by dentate tartrate ligands. The Strontium Tartrate Complexes were synthesized by a simple co-precipitation method and then purified. The said complexes were characterized using X-ray diffraction, UV visible, IR and Raman spectroscopy. The XRD analysis showed that the complexes are having polycrystalline nature. The UV visible spectroscopy showed that the Strontium Zinc and Strontium Cobalt tartrate complexes have very high UV absorption in certain windows and therefore they can be used in design and development of UV filters. The IR analysis in consistent with Raman analysis showed stretching of C-H, C-O, C=C and C≡C bonds representative sp^2 and sp^3 hybridized carbon atoms. The anti-microbial activity of all the four complexes have been studied with S. Aureus and E. Coli bacteria and the results showed that S. Aureus bacteria is more sensitive to the complexes than E. coli. By and large the Strontium tartrate complexes have shown their ability to be used in formulating drugs against bacteria. Details are presented.

Keywords: Strontium Tartrate Complexes, Antimicrobial Activity, UV Filters, Raman Spectroscopy, Coprecipitation Method.

1. INTRODUCTION

In last decade the use of tartrate complexes for several applications has attend the interest of many researchers working in the field of material and biological sciences, medicinal chemistry, and physical sciences [1-4]. The use of sodium tartrate complexes in making of ferroelectric device has been demonstrated by Gon et al [5]. In study carried out by Betallu et al the antimony barium tartrate was used as a veterinary drug [6]. Few researchers have studied the thermal properties of calcium tartrate [7,8]. Further there are a few reports which shows the use of tartrate complexes exhibits piezoelectric behavior and magnetic hysteresis [9,10]. The materials like graphene and various type of nanocarbons because of their extraordinary physical and chemical properties can be used together with tartrate complexes for various applications [11-22]. Soma et al has studied the calcium tartrate complexes and their use for biological activity to assess their antibacterial and antifungal effects [23,24]. There are a few reports where dicarboxylate ligand and their metal complexes were used as an antimicrobial agent [25-28]. However not much attention has been paid on studies related to use of various combination of mix metal ligand complexes for the antimicrobial applications. The present study deals with the synthesis, characterisation and evaluation of strontium tartrate complexes for antimicrobial activity with Staphylococcus Aureus (S. Aureus) and Escherichia coli (E. coli) bacteria. Details are presented.

2. MATERIAL AND METHODS

1.1. Preparation of Strontium tartrate complexes by Co-precipitation method

To synthesize strontium tartrate complexes we have used hydrated metal salt ($SrCl_2.6H_2O$, $ZnCl_2.2H_2O$, $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, and $MnCl_2.4H_2O$) of AR grade. The distilled water was used as a solvent and a simple co-precipitation technique was followed [29,30]. To begin with the aqueous solutions of $SrCl_2.6H_2O$ and $CoCl_2.4H_2O$ were admixed in equal molar ratio. The pH of the solution is maintained below 6 so as to restrict the formation of hydroxide precipitate. The solution was continuously stirred with the help of magnetic stirrer at 60^0C. then Sodium tartrate (15%) solution was gently added while continuous stirring was going on till the formation of permanent precipitate. Post this the precipitate was filtered and separated. Then the precipitate was repeatedly washed with acetone and then kept in desiccators**.** Post this the as synthesized material samples were subjected to annealing in vacuum oven at 100^0C for two hours so as to remove any impurity present in the said materials and then the purified material samples were allowed to cool naturally. Then the prepared material was named as Strontium Zinc tartrate complex ($SrZn(C_4H_4O_6)_2.xH_2O$). In similar way the remaining three Strontium tartrate complexes were prepared.

1.2. Characterization techniques used: To study the structure property relationship the as synthesized material was subjected to various characterization techniques including X-ray diffraction (BRUKER D8 Advance) UV visible spectroscopy (JASCO UV-Visible 670), IR spectroscopy (BRUKER FTIR) and Raman spectroscopy (HORIBA HR 800). Suitable samples have been prepared and they were subjected to above characterization techniques.

1.3. Antimicrobial activity: The antimicrobial activity was perform with the help E.Coli and Staphylococcus Aureus. Initially the bacteria culture was grown and taken in Agar plates. In each such plates 0.5 ml of bacterial culture of E.Coli and Staphylococcus Aureus was dispersed uniformly on the surface and then subjected to incubation for half hour at 40^0C so that the bacterial culture may get absorbed on the surface of the medium. With the help of well borer 03 wells were bored with 0.1 ml of tartrate complexes solution was poured in each well

and subjected to incubation at 5^0C for one hour duration such that it should get diffused properly. Then all such plates were again subjected to incubation for 48 hours and then zone of inhibition for each tartrate complexes solution was record.

3. RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

The purified powder samples were characterized using X-ray diffraction technique and recorded patterns are shown in Figure 1. In analysis all the four Strontium tartrate complexes showed polycrystalline nature. The particle size was estimated using the $D = 0.89\lambda / \beta \, Cos\Theta$ relationship. The estimaed d spacing for $SrZn(C_4H_4O_6)_2.xH_2O$, $SrCu(C_4H_4O_6)_2.xH_2O$, $SrCo(C_4H_4O_6)_2.xH_2O$, and $SrMn(C_4H_4O_6)_2.xH_2O$ is found to be $1.349A^0$,$4.782A^0$, $5.995A^0$, and $5.878A^0$ respectively.

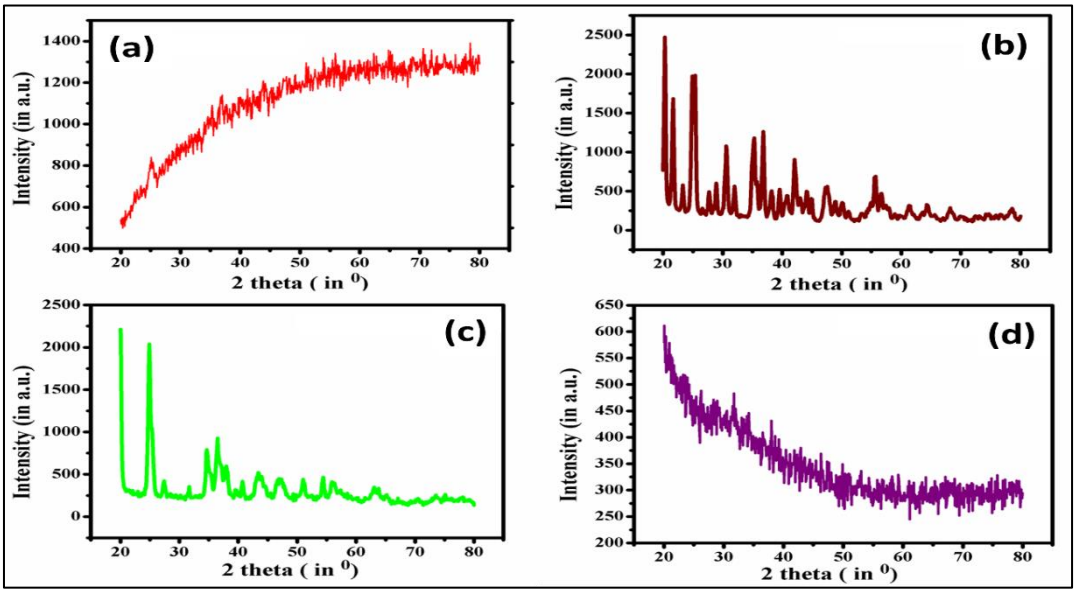

Figure 1: Recorded X ray diffraction pattern for (a) $SrZn(C_4H_4O_6)_2. H_2O$, (b) $SrCu(C_4H_4O_6)_2. H_2O$,(c) $SrCo(C_4H_4O_6)_2. H_2O$, and (d) $SrMn(C_4H_4O_6)_2. H_2O$.

UV visible Spectroscopy Analysis

As shown in Figure 2, the UV visible spectra recorded for (a) Strontium Zinc complexes showed that very high absorption for the wavelength windows ranging from 200 to 270 nm and 390 to 570 nm indicating that the material can be used for UV filtering. The estimated bandgap (E_g) for this complex is 4.57 eV giving indication about the insulative nature of the Strontium Zinc complex. In figure (b) recorded for Strontium Copper complexes the material has shown higher UV absorption percentage for 700 to 800 nm range and the estimated E_g is found to be 3.61 eV commenting the semiconductor nature of the complex. The Figure (c) Strontium Cobalt complex shows higher absorption of UV wavelength in the range of 490 to 610 nm and the estimated E_g is 4.5 eV suggestive of semiconductor behavior of the complex. As shown in the figure (d) the Strontium Manganese complex shows no significant absorption windows of UV frequencies, the estimated E_g is found to be 4.7 eV. Moreover, one can say that the Strontium Zinc and Strontium Cobalt complexes can be used for the design and development of UV filters for specific ranges.

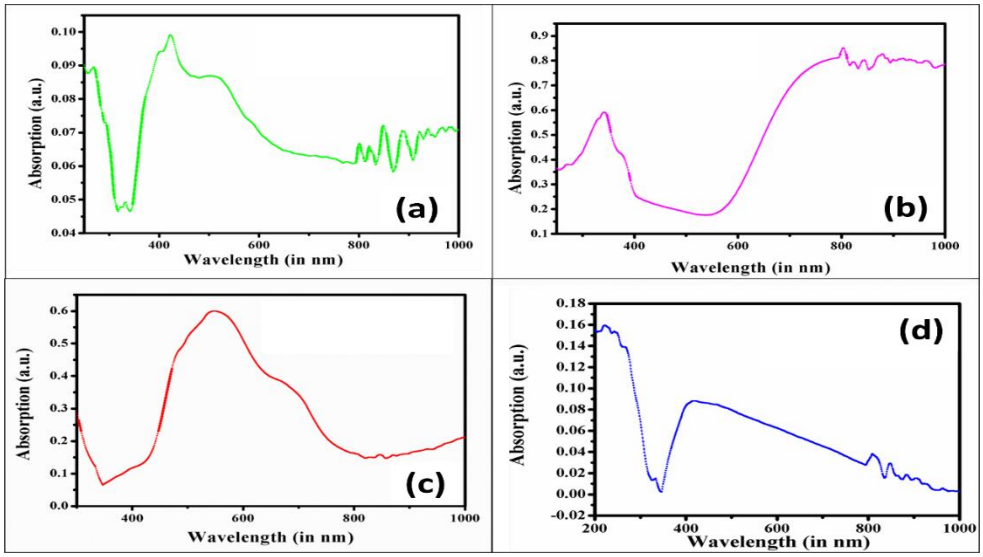

Figure 2: UV visible spectra recorded for (a) $SrZn(C_4H_4O_6)_2.H_2O$, (b) $SrCu(C_4H_4O_6)_2.H_2O$,(c) $SrCo(C_4H_4O_6)_2.H_2O$, and (d) $SrMn(C_4H_4O_6)_2.H_2O$.

Infrared (IR) Spectroscopy Analysis

To understand and verify the compositions and structure property corelation IR spectroscopy studies were performed. Figure 3 shows the IR spectrograph recorded for (a) Strontium Zinc complex shown stretching of C-H, C-O and O-H bonds at 2983 cm^{-1} 1367 cm^{-1} and 1087 cm^{-1} respectively. Further signatures of the impurities like Nitrogen, Sulphur and halogens (Bromine and Iodine) were seen at 3404 cm^{-1}, 928 cm^{-1} and 637 and 556 cm^{-1} respectively. In (b) Strontium Copper complex have shown C-H, C-O and C=C stretches at 1608 cm^{-1} ,1272 cm^{-1} and 885 cm^{-1} respectively. Similar to the Zinc complex this complex also shows the presence of impurities like Nitrogen, Sulphur, Bromine and Iodine at 3411 cm^{-1}, 1221 cm^{-1}, 640 cm^{-1},533 cm^{-1} respectively. The Figure (c) and (d) corresponding to Strontium Cobalt and Strontium Manganese complexes shows the signatures of O-H and C=C stretching at 1420 cm^{-1} and 893 cm^{-1} respectively. The impurities like Nitrogen, Sulphur, Bromine and Iodine were also seen. The presence of this common impurities in all the complexes is due to the coprecipitation technique of synthesis used and there after ineffective use of purification techniques.

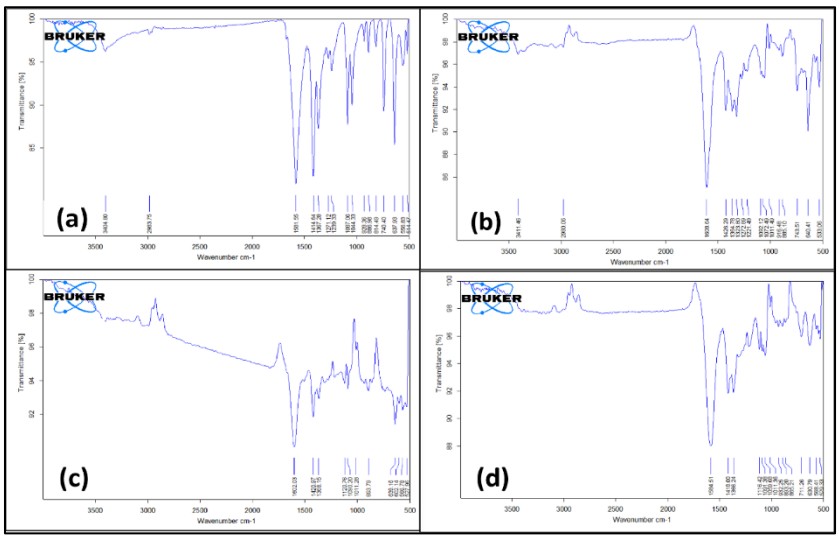

Figure 3: IR spectrographs recorded for (a) $SrZn(C_4H_4O_6)_2.H_2O$, (b) $SrCu(C_4H_4O_6)_2.H_2O$,(c) $SrCo(C_4H_4O_6)_2.H_2O$, and (d) $SrMn(C_4H_4O_6)_2.H_2O$

Raman Spectroscopy Analysis

Raman spectroscopy is nondestructive tool to study the phonon vibrational modes, elemental analysis, presence of bonds, bond length, stresses, electron phonon coupling, estimation of force constant, impurities present, and estimation of number of layers in the given material. However, one has to pay a cost of it by doing rigorous analysis of the obtained Raman data.

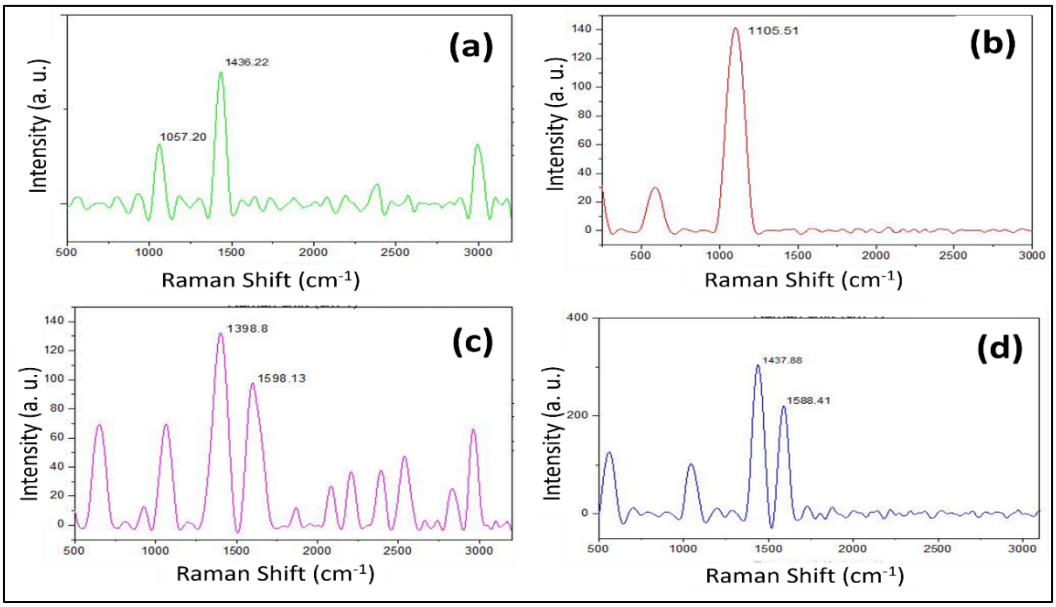

Figure 4: Raman spectrographs recorded for (a) $SrZn(C_4H_4O_6)_2.H_2O$, (b) $SrCu(C_4H_4O_6)_2.H_2O$,(c) $SrCo(C_4H_4O_6)_2.H_2O$, and (d) $SrMn(C_4H_4O_6)_2.H_2O$

The Figure 4 shows the Raman spectrograph recorded for (a) Strontium Zinc complex shows the stretching of C-H bond at 1436 cm^{-1} and O=C=O at 2400 cm^{-1} further it also shows the presence of impurities like sulphur and nitrogen at 1057 cm^{-1} and 3000 cm^{-1} respectively. No significant signature of Zn was observed. In (b) Strontium Copper complex shown dominant signature of impurities of halogens (iodine and fluorine) bonded with carbon are seen at 600 cm^{-1} and 1105 cm^{-1} respectively. Figure (c) the spectrograph for Strontium Cobalt complex shown the presence of sp^2 hybridized C=C and sp^3 hybridized C≡C at 960 cm^{-1} and 2100 cm^{-1} respectively. The signature of stretching of C-O, C-H and O=C=O bonds were seen at 1100 cm^{-1}, 2800 cm^{-1} and 2380 cm^{-1} respectively. In (d) Strontium Manganese complex the halogen impurities like Iodine and Fluorine singly bonded with Carbon has been observed at 550 cm^{-1} and 1080 cm^{-1} respectively. The presence of the above impurities is one the drawback of coprecipitation technique. In order to remove such impurities, one may follow the intercalation, annealing and vacuum filtration purification methods. By and large the Raman analysis of the above said complexes confirmed the coupling of metal ions at donor sides of the legend.

Anti-Microbial Activity

All the above said complexes have been evaluated for anti-microbial activity with the procedure as specified in section 2.3 with Staphylococcus aureus and E. coli. The Figure 5 (a) and (b) represents the antimicrobial activity images showing zone of inhibition for the three Strontium metal complexes (Strontium Manganese, Strontium Copper, Strontium Cobalt respectively).

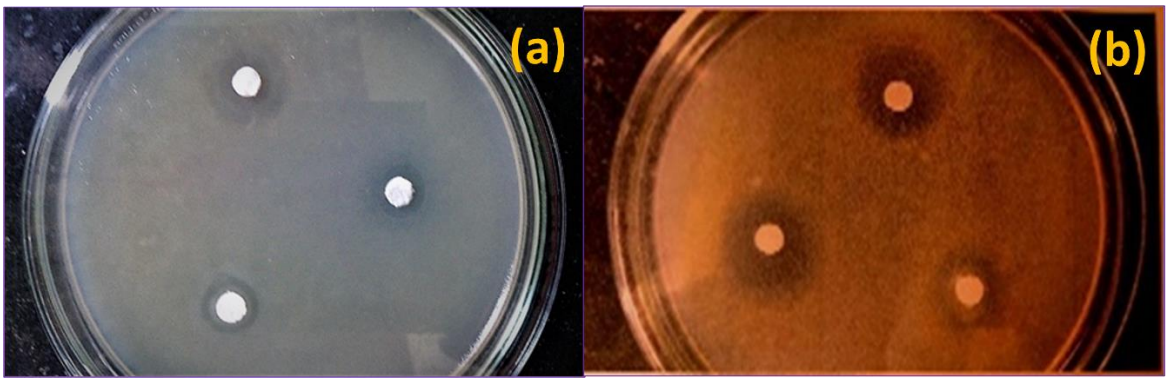

FIGURE 5: (a) Antimicrobial activity of $SrCu(C_4H_4O_6)_2.xH_2O$, $SrCo(C_4H_4O_6)_2.xH_2O$,and $SrMn(C_4H_4O_6)_2.xH_2O$ with (a) E. coli, (b) S. Aureus.

Table 4: Antibacterial activity studies of complexes: [zone of inhibition (in mm)]

Sr.No.	Name of Complex	E. Coli	S. Aureus
1	$SrCu(C_4H_4O_6)_2.\ xH_2O$	8	13
2	$SrCo(C_4H_4O_6)_2.\ xH_2O$	10	25
3	$SrMn(C_4H_4O_6)_2.\ xH_2O$	6	9

The table 1 represents the measured inhibition zone (in mm) with respect to the complexes and both the bacteria. It can be clearly seen and shown that the inhibition zones recorded for the complexes in figure (a) for E. Coli bacteria are comparatively smaller (6 to 10 mm) than the inhibition zones recorded for the complexes in Figure (b) for S. Aureus bacteria (9-25 mm) respectively. The strontium Cobalt complex have shown the highest inhibition zones for both the bacteria with 10 mm for E. Coli and 25 mm for S. Aureus. The anti-microbial activity shown by these metal complexes may be due to chelation of metal ions with tartrate legend that may have given rise to delocalization of π-electrons in the chelate ring and that may cause increase in lipophilicity which may further lead to enhancing the capability of the complex to penetrate in the lipid membranes of the microorganisms and this slows down the respiration process. This further leads to creating hurdles and blockages in synthesis of proteins which restricts the growth of bacteria. in a nut shell one can say that the Strontium complexes have the ability to be used in formulating drugs against bacteria's and Strontium Cobalt complex is the best fit for the same.

4. CONCLUSION

In the present paper four strontium tartrate metal complexes ($SrZn(C_4H_4O_6)_2.xH_2O$, $SrCu(C_4H_4O_6)_2.\ xH_2O$, $SrCo(C_4H_4O_6)_2.\ xH_2O$, and $SrMn(C_4H_4O_6)_2.xH_2O$) have been prepared using a simple co- precipitation technique and then subjected to annealing for purification. To study the structure property relationship the purified materials were subjected to X-Ray diffraction, UV visible, IR and Raman spectroscopy. In XRD analysis the recorded patterns showed that the complexes are having polycrystalline nature with d spacing ranging from 1.349 A^0 to 5.878 A^0. The UV visible spectroscopy showed that the Strontium Zinc tartrate complexes have very high UV absorption in certain windows and therefore they can be used in design and development of UV filters. On the basis of the estimated band gaps the Strontium Zinc and Strontium Manganese tartrate complexes have shown insulating nature whereas the Strontium Copper and Strontium Cobalt complexes have shown semiconductor nature. The IR analysis showed that in almost every complex stretching of C-H, C-O and C=C bonds have been observed. The Raman spectroscopy analysis was consistent with IR analysis and prominent peaks of C-H, C-O, C=C and C≡C are found which are representative sp^2 and sp^3 hybridized

carbon atoms. Further, presence of impurities like Nitrogen, Sulphur, Bromine and Iodine have been noted in Raman and IR analysis. The overall analysis showed that there is need of further purification when the materials are synthesized with co-precipitation technique. The anti-microbial activity of all the four complexes have been studied with S. Aureus and E. Coli bacteria and the inhibition zones recorded for E. coli (6-10 mm) bacteria are comparatively smaller than that recorded for S. Aureus (9-25 mm). The Strontium Cobalt tartrate complex have shown highest anti-microbial activity with inhibition zone of 10 mm with E. Coli and 25 mm with S. Aureus. By and large the Strontium tartrate complexes have shown their ability to be used in formulating drugs against bacteria.

Conflict of Interest
There is no conflict of Interest.

Author Contributions
Ms. Rohini Gawade, Ms. Reeya Narsinghani and Dr. Shamal Chinke incepted the idea and performed the synthesis of materials. The characterizations were performed by Ms. Rohini Gawade, Ms. Reeya Narsinghani, Dr. Sandeep Palve and Dr. Kailash Sapnar. The data analysis and manuscript writing were done by Ms. Rohini Gawade, Ms. Sanika Aywale and Dr. Shamal Chinke.

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