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Synthesis of Manganese complexes of tannic acid in green method.

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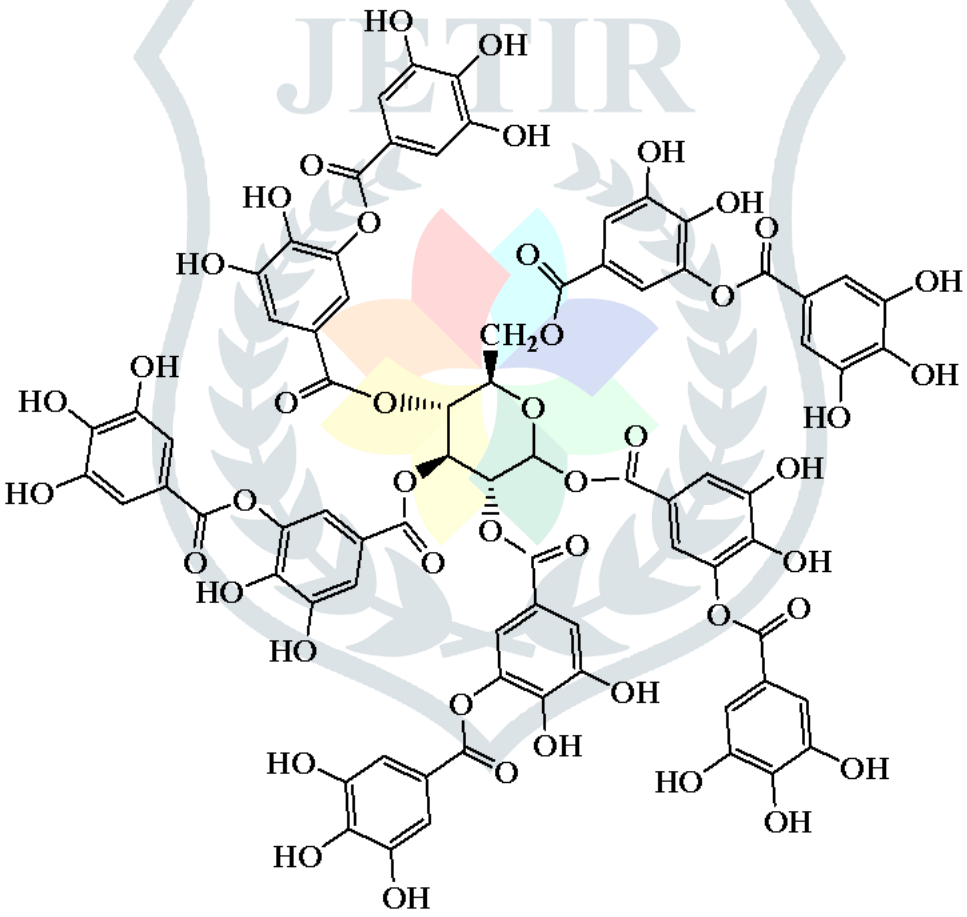
Abstract: Tannic acid is a specific commercial form of tannin, a type of polyphenol. Its weak acidity (pKa around 10) is due to the numerous phenol groups in the structure. The chemical formula for commercial tannic acid is often given as $C_{76}H_{52}O_{46}$. Its structure is based mainly on glucose esters of gallic acid. It is a yellow to light brown amorphous powder which is highly soluble in water. Tannic acid is a basic ingredient in the chemical staining of wood. The tannic acid or tannin is already present in woods like oak, walnut, and mahogany. Today tannic acid is used in pharmaceutical applications to produce albumine tannate which is used as an anti-diarrhea agent. They found that Tannins have also been reported to exert many physiological effects, such as to accelerate blood clotting, reduce blood pressure, decrease the serum lipid level, produce liver necrosis, and modulate immune responses. Tannic acid due to its extensive donating centers can act as very good chelator. Already tannic acid complexes of copper and Iron were reported. In diagnostic medical science tannic acid is used for detecting peptic ulcer where Technetium-99m is used as the main radio active metal. In this work Mn complexes of tanic acid has been synthesized as Mn belong to the same group of Tc. The Complex is polymeric in nature which is insoluble in all common solvents. The complex is paramagnetic with only one unpaired electron which was proved by electron spectra

Introduction: Tannic Acid (TA) is a naturally occurring antioxidant polyphenol that has gained popularity over the past decade in the field of biomedical research for its unique biochemical properties. Tannic acid is a specific commercial form of tannin, a type of poly phenol. It's weak acidity is due to the numerous phenol groups in the structure. The chemical formula of commercial tannic acid is often given as $C_{76}H_{52}O_{46}$. Its Structure is based mainly on glucose ester of gallic acid. It is a yellow to light brown amorphous powder which is highly soluble in water. Tannic acid, typically extracted from oak tree galls, has been used in many important historical applications [2,3,4]. TA is a key component in vegetable tanning of leather, iron gall ink, red wines, and as a traditional medicine to treat a variety of maladies. The study of TA has led to the development of many new pharmaceutical and biomedical applications. TA has been shown to reduce

inflammation as an antioxidant, act as an antibiotic in common pathogenic bacterium, and induce apoptosis in several cancer types[5,6,7,8]. TA has also displayed antiviral and antifungal activity. At certain concentrations, TA can be used to treat gastrointestinal disorders such as haemorrhoids and diarrhoea, severe burns, and protect against neurodegenerative diseases. TA has also been utilized in biomaterials research as a natural crosslinking agent to improve mechanical properties of natural and synthetic hydrogels and polymers, while also imparting anti-inflammatory, antibacterial, and anticancer activity to the materials. TA has also been used to develop thin film coatings and nanoparticles for drug delivery. In all, TA is fascinating molecule with a wide variety of potential uses in pharmaceuticals, biomaterials applications, and drug delivery strategies.

Tannic acid is used in pharmaceutical applications to produce albumin tannates which is used as an anti-diarrhea agent. Tannic Acid due to its extensive donating sites can act as a very good chelator. Already tannic acid complexes of copper and iron are reported [1]. In diagnosis medical science, tannic acid is used for detecting peptic ulcer where technetium-99m is used as the main radioactive metal. My aim is to determine the manganese complexes of Tannic acid as both Manganese and Technetium are in same group. I tried to prepare the complex in green method as this method saves energy. Green techniques have been widely reported as potential approaches for the synthesis of inorganic complexes, with the results being shown to be safe and environment friendly . Tannic acid (TA) is a natural polyphenol and one of the cheapest natural abundant functional materials [9,10]. Its five pyrogallol and five catechol groups provide multiple bonding sites with diverse interactions, such as ionic, coordination, hydrogen bonding, and hydrophobic interactions [11,12,13]. Its oxygen-rich functional groups, which include catechol and pyrogallol groups, can coordinate with variety of transition metal ions, forming coordination complexes. They possess metal–phenolic coordination and have been explored in the past [14,15,16,17,18]. A variety of metal–tannate coordination complexes and polymers have been applied as either thin films or particles with tailored properties [14] or in the formation of novel metallogels [17]. The use of TA as either porogen or an additive component in materials science has attracted great attention. This is due not only to its cheap, environmentally friendly, and nontoxic nature, but also its ability to be used as a non-surfactant template. For example, past research has demonstrated that TA can be used as a porogen to tune the porosity of other inorganic particles and make mesoporous materials with tunable mesopore sizes ranging from 6 to 13 nm [19,20,21,22,23]. The

coordination complex formation between tannic acid and iron(III) was demonstrated recently, albeit in a very few literature reports [24,25,26,27,28]. A supramolecular assembly of iron(III)-tannic acid metal–organic complex was developed as an antimicrobial spray nanocoating. It has demonstrated its utility as an antimicrobial coating in shoe insoles and fruits [24]. Additionally, a molecular nanoparticle-based Fe(III)-tannic acid complex was previously synthesized using a low-cost, reproducible method and its physicochemical properties (including its capability of inducing autophagy effect in two selected liver cell lines) were studied [25,26,27,28]. Furthermore, a self-assembly of metal ions with tannic acid on various substrates was demonstrated using coordination programming to prepare multifunctional thin films and capsules [29,30,31,32,33].



Experimental

Material

All the chemicals used in this work were of analytical grade available commercially and were used without further purification.

Physical Measurement

Infrared Spectra were recorded on a Jasco-5300 FT-IR spectrophotometer by using KBr pellets. A perkin Elmer Lamda 35 UV/vis spectra. Magnetic susceptibility balance was used to measure the magnetic susceptibility.

Synthesis of Mn(TA) Complex

To a stirring solution of tannic acid (0.1703 gm, 0.0001 mol) in methanol (15 ml) , sodium acetate solution (0.496 g , 0.0006 mol in 10 ml methanol) was added, followed by the addition of potassium permanganate solution (0.60 g, 0,0004 mol) in 5 ml methanol. The whole mixture was stirred for one hour . A black solid complex was formed. It was filtered . The residue was washed with methanol again and it was dried in air.

Results and Discussions

The complex was synthesized in good yield (80-90 %) .The complex **was** black coloured hard solid and insoluble in all common solvents .The complex was first analysed for magnetic susceptibility in the magnetic susceptibility balance .The result showed that the complex is paramagnetic in nature with magnetic susceptibility value 1.41×10^{-5} .

Spectroscopic Properties

ESR spectrum with only one single peak suggest that the presence of only one unpaired electron .

Infrared spectra (fig 2-30 of all the compounds have been recorded using KBr pallets .Free tannic acids contain hydroxyl group as well as ester carbonyl functions which can bind metal ions .Stretching frequency for the hydroxyl group is around 3550-3200 cm^{-1} (broad ,s) and in both the figures it is same from which it is concluded that the possibility is tannic acid is not forming any bond with metal ions through the hydroxyl group .Stretching frequency for the carbonyl group of ester function is around 1750

-1735 cm^{-1} (s) which is reflected in the IR frequency chart of tannic acid as peak 2,3,4,5 .These peak intensities get reduced in the IR frequency chart of the Mn complex chart indicates that the tannic acid has from the complex with Manganese metal through ester carbonyl group.

In potassium permanganate is present in +7 oxidation sate and its electronic configuration is s^2d^5 .When it is in +7 oxidation state therefore it is expected that the complex will be diamagnetic .But the prepared complex is paramagnetic in nature with only one unpaired electron .Therefore it is assumed that tannic acid reduced the manganese metal by donation one electron .

The complex was insoluble in all common solvents which suggest that it is polymeric in nature .It is amorphous and so it was not possible to determine the structure of the complex.

Conclusion

In conclusion we have synthesised and characterise a manganese complex of tannic acid which is polymeric and paramagnetic in nature .It is probably forming complex with tannic acid and ester carbonyl function .

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