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ORIGINAL RESEARCH ARTICLE

Study on Metal Complexes of Gallate

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ABSTRACT

In this paper, the electrochemical properties of copper alloy isoamylate gallate were studied by cyclic voltammetry. The structure of the complex was analyzed by infrared spectroscopy. The infrared spectra show that the metal ions interact with the phenolic hydroxyl groups. The results of cyclic voltammetry show that the conjugation system increases and the electron cloud density decreases, and the electrons are larger in the whole molecule, and are more likely to lose electrons, and thus have higher redox activity.

Keywords: Isoamyl Gallate Metal Copper Complex; Cyclic Voltammetry; Infrared Spectroscopy

1. Introduction

Coordination Compounds (Complex Compounds), also known as complex (Complex Compounds), referred to as complexes, mainly refers to the electron pair or several sub-regional electron vacancies with atoms or ions as the center, with a group can give electrons a compound of a molecule or a plurality of indefinite electrons or a ligand (ligand) that is characterized by a certain spatial structure in the surrounding individual. It has been over a hundred years since Verne found the theory of coordination in 1893[1]. Coordination chemistry is an edge discipline of inorganic chemistry, organic chemistry, physical chemistry, biochemistry, medicinal chemistry, solid chemistry, environmental chemistry, materials chemistry and materials science. The basic task is the study of interaction of phenomenology and molecular, Atomic level, metal and ligand (including organisms such as proteins, nucleotides and sugars, etc.); and the structure and application of complexes[2]. In recent years, coordination chemistry has opened up research fields such as macrocyclic complexes, supramolecular chemistry, molecular recognition, functional complexes, porphyrin complexes, transients and C60 complexes. Coordination chemistry is widely used, such as catalysis, biochemistry, pharmacology, fiber dye chemistry, rare metal smelting, photography, electroplating and waste treatment[3].

Pyrogallol derivatives mainly include gallic acid, gallate, tannic acid and tea polyphenols. Gallic acid (Gallic acid), also known as 3,4,5-trihydroxybenzoic acid, gallic acid. 3,4,5-trihydroxybenzoic acid monohydrate ($C_7H_6O_5 \cdot H_2O$), a pair of phenolic hydroxyl groups in the gallic acid molecule to form intramolecular hydrogen bonds, and a molecular water to form three centers of OH-H ... O hydrogen bonds. Each gallic acid monohydrate molecule is interconnected by O-H ... O and C-H ... O bonds to form crystals. Gallic acid is white or light brown needle-like crystals or powder; melting point 235-240 0C (decomposition), heated to 100-120 0C loss of crystal water, heated to 2000C above the formation of pyrogallic acid (pyrogallol); dissolved in hot water, ether, ethanol, acetone and glycerol, insoluble in cold water, insoluble in benzene and chloroform. Gallic acid is obtained by gallnut. Gallic acid can be obtained by esterifi cation or through the role of enzymes can be obtained gallate, propyl gallate, butyl gallate and other gallate, the basic structure shown in **Figure 1**[4-6].

A large number of phenolic hydroxyl groups in the pyrogallol derivatives make it complex with most of the trivalent metal ions and transition metal ions, which are common to phenolic compounds. The coordination occurs mainly on two adjacent phenolic hydroxyl groups of the pyrogallol derivative molecule, in which the

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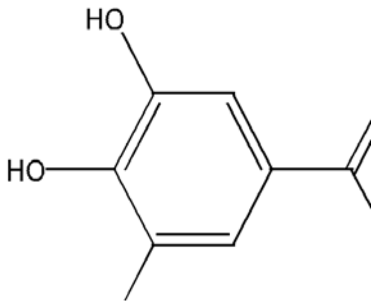

Figure 1. Structure of gallic acid or gallate (R = H, gallic acid; R = X, gallate).

third phenolic hydroxyl group of the pyrogallol derivative does not participate in the coordination but promotes the activation of the other two phenolic hydroxyl groups dissociation makes the coordination more stable[7].The function of coordination, adsorption and reduction of heavy metal in pyrogallol derivatives has a good effect on alleviating the toxicity of heavy metals. Polyphenols and metal ions Mn + form ligands depending on the proportions of the components of the various pyrogallol derivatives, the structure of the reaction product that may be produced is shown in **Figure 2**.

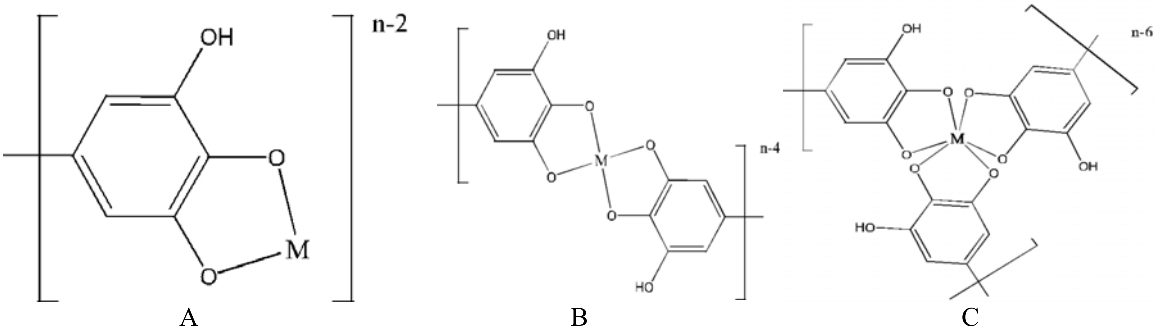

Figure 2. Possible structure of polyphenolic metal complex (a: single coordination, b: double coordination, c: three coordination)

When the pyrogallol derivative reacts with the metal ion, H+ is released and the pH of the system is reduced. General improves the pH of the system is conducive to complexation, but at higher pH conditions, on the one hand even pyrogallol derivatives easily oxidized into quinone, so that the loss of phenoxy ligands. On the other hand, the hydrolysis of metal ions will be enhanced, so that the balance of the reaction system move the direction of hydrolysis, making the coordination bond fracture, and the formation of hydroxide precipitation. At the same time, the coordination number of some benzodiphenolic derivatives metal complexes depends on the pH of the reaction system. For metal ions with high oxidizing properties, the pyrogallol derivatives also exhibit strong reducing properties, and the high valence metal ions are reduced to the low valence state in the event of complexation reaction.

2. Topic background

2.1. Source of the project

In 2005, the group led by Souza (Spectral and Electrochemical Properties of Al (III) and Zn (II) Complexes with Flavonids from Spectrochim Acta: Part A) validated the antioxidant strengths of polyphenols and their complexes. The lower the potential, the better the antioxidant performance, which provides a theoretical basis for the study of the changes in the antioxidant properties of the gallate metal ligands.

In addition, two studies, from the electrochemical studies of propyl gallate metal complexes from the Institute of Applied Chemistry, Wuhan University of Science and Technology in the past three years, have shown that the study of gallate metal complexes is feasible and shows that units of this series of compounds research work is being carried out. At the same time, the process of this study is relatively simple, suitable for the removal of part of the chapter as a graduate design research topics, but also as a series as a graduate student issues. Finally, this experiment requires the use of the compound structure verification device for Fourier infrared, electrochemical workstation.

2.2. Purpose and meaning of the study

The pyrogallol and its complex not only have antibacterial, anti-cancer, inhibit oxygen free radicals and other biological activity, it also has antioxidant, corrosion and electrostatic effects and other characteristics. It has a wide range of applications, making it with practical significance to study the synthesis, structure, properties and application of this kind of compounds.

In this paper, a simple structure of simple pyrogallol-based isobutyrate isopentylate was synthesized. The novel pyrocatecholate complex was synthesized and its electrochemical properties were tested. The structure of the compound was studied and the results were as follows. Theoretical guidance.

2.3. Research progress

Gallic acid can be used as an extractant and a detection reagent[8]. You can use gallic acid to extract a variety of rare metals, such as germanium, tantalum, niobium and so on. It can also be used to detect antimony, bismuth, calcium, barium, cerium, copper, zinc, aluminum and many rare elements. In 2001, Nanjing University of Chemical Engineering, Song[9] and others used $HClO_4$ to support the electrolyte, gallic acid taste complex agent, in the oscillopolarographic germanium on the determination of germanium determination of the linear range is 2.0 × 10-6 -5.0 x 10-5 mol/L. The molar ratio of Fe^{2+}, Al^{3+}, 16 times Ni^{2+}, and 10 times Zn^{2+} and Pb^{2+} did not interfere with the determination. The experimental results showed that the ratio of the complex was 1:2. (IV)-gallic acid in the dilute sulfuric acid medium by adding vanadium (IV) and EDTA to produce a high sensitivity complex adsorption parallel catalytic current, so that germanium (IV)-gallic acid in dilute sulfuric acid medium. The adsorption current is more than 1200 times, which is used for the determination of trace germanium in the superalloy. The results are consistent with the photometric method and ICP-MS. Jiang *et al.*[11] and other uses in the pH buffer of the buffer solution of acetic acid, germanium (IV)-gallic acid-vanadium (V)-EDTA system to produce sensitive adsorption parallel catalytic wave potential measurement in mineral water Trace germanium. Long[12] and team use pH 2.6 in the chloroacetate buffer solution, tin (IV)-gallic acid-vanadium (IV) system to produce sensitive adsorption parallel catalytic wave potential determination of trace tin in food.

Gallic acid can be used as raw materials to produce sulfonamides synergist TMP, anti-schistosomiasis double gallic acid antimony, antiseptic bismuth gallate and so on. Zhang[13] and other gallic acid and antimony potassium tartrate as raw material synthesis of basic gallic acid antimony, and elemental analysis, infrared spectroscopy, thermal analysis and other methods were measured.

In recent years, the coordination behavior of gallic acid and metal has been studied theoretically, and the biological activity of its complex has also been studied. ($C_{12}H_8N_2$) ternary complex and Cu^2+, Ni^{2+} and gallic acid, 2,2-bipyridine ($C_{10}H_8N_2$) tris Meta-complexes; and their structures were characterized. Nakayausu and other studies have found that organic carbon substances such as humic acid, tannic acid, gallic acid can be hexavalent Cr into trivalent Cr, to achieve the degradation of hexavalent Cr. During this reaction, the chemical reaction kinetics of tannic acid and gallic acid is 2-3 orders of magnitude higher than that of humic acid. As a result, the reduction of hexavalent chromium in the reaction process, tannic acid, gallic acid to form a polymer, reduction of Cr (III) with tannic acid, gallic acid polymer coordination; after reduction of Cr (III) And tannic acid, gallic acid formation complexes than humic acid. Above The results are shown in the data of ultraviolet-visible spectroscopy and gel permeation chromatography.

The structure and reaction mechanism of Mairtin and Michael on the reaction of Al (III), Fe (III) with gallic acid and methyl gallate to form complexes were studied. Arif and other people think that gallic acid is caused by excessive drinking tea, the reasons for iron deficiency were studied. At pH 4-6, a part of the acid and iron can form a 3:1 complex, which is decomposed gradually under the action of ascorbic acid. The decomposition rates at pH 4, 5, 5, and 5.4 were 30 M-1S-1, 21.5 M-1S-1 and 9.4 M-1S-1 at 30 °C, respectively. In 2001, Arakawa H *et al*. Cr (III) and gall (III)-gallic acid (Cr (III)-gallic acid, Cr (III)-gallic acid methyl ester; Cr (III) The results showed that the complexes of Cr (III)-gallic acid, Cr (III)-gallic acid methyl ester were DNA ($P < 0.05$), and the interaction between gallic acid, Cr (III)-methyl gallate and calf thymus DNA was analyzed. External bonding material cannot form a chelate bond with DNA. 2004 Gerasymchul YS and other studies have found that phthalocyanine blue and phthalocyanine hafnium with gallic acid, 5-sulfonic acid salicylic acid, oxalic acid, gallic acid methyl ester axial coordination of water-soluble axial Complexes. The complexes of this type of complexes in different solvents have characteristic absorption spectra. At the same time, the fluorescence properties of the complexes in DMSO are studied.

In 2004, in the study of the coordination behavior of zinc (II) gallic acid and its interaction with DNA, the concentration of gallic acid was fixed and the concentration of Zn^{2+} was changed. The contents of gallic acid and Zn^{2+} binary complexes. And the use of benzoic acid (carboxyl), pyrogallol (3 phenolic hydroxyl) and methyl gallate (carboxyl protected 3 phenolic hydroxyl) and Zn^{2+} reaction experiments. The results showed that the absorption spectra of benzoic acid after adding Zn^{2+} did not change, while pyrogallol and methyl gallate had similar red shift and isotonic point of Zn^{2+} reaction with gallic acid. This indicates that only the hydroxyl group participates in the coordination process during the reaction. The coordination bond is the main force of the action of gallic acid and Zn^{2+}. The coordination ratio in the process is 1:1. It is also pointed out that the role of GA-Zn^{2+} complex with DNA is mediated by the electrostatic interaction of Zn^{2+} with DNA molecules. Subbarao M and Srinivasulu K studies have found that gallic acid and 1,2-diaminocyclohexane tetraacetic acid can form niobium with gallic acid and gallic acid and l, 2 at 25 °C in tartrate solution at pH = 2.5. Synthesis of complexes of diaminocyclohexane tetraacetic acid. The complexes were characterized by UV absorption spectroscopy at 470 nm. Fare M study in 1997 found that under aerobic conditions, gallic acid with Fe^{2+} coordination, the formation of ferrous gallate complexes, but ferrous gallate complexes will be oxidized into soluble iron gallate complex.

The esterified derivatives of gallic acid are mainly methyl gallate, propyl gallate and octyl gallate. Propyl gallate, also known as Tongmai ester, red peony 801. Propyl gallate is used as an antioxidant in cosmetics and food at home and abroad. At the same time as propyl gallate has anti-free radical, anti-inflammatory, blocking lipoxygenase activity, anti-platelet aggregation, stimulation of platelet granule release agent changes platelet membrane composition and other pharmacological activity, propyl gallate is a for prevention and the treatment of cerebral thrombosis, coronary heart disease and thrombophlebitis and other thrombotic diseases of drugs[16].

Li[17] and other synthetic in addition to Sn (IV) and propyl gallate 1:1 type of complex, and chemical adsorption stripping voltammetry carried out a preliminary study. Studies have shown that the complexation of gallic acid occurs mainly in the two phenolic hydroxyl groups. Holder *et al*. used the method of removing metal surface oxides and corroded sediments by chelating the pyrophenol and methyl gallate with metal under the condition of pH 6.5-7.5. (Ti) and X-ray diffractometry (XRD) were used to study the synthesis of complexes and their catalytic properties. The results showed that the Pb(II)-gallate complex was prepared by liquid phase dispersion precipitation method.

2.4. Outlook

Plant polyphenols are of certain medicinal value, and they are effective in preventing cell aging and are currently reported as cardiovascular and viral diseases and treatment of cancer outcomes. Gallic acid ester as a plant polyphenols, has a certain antioxidant properties, is a mature oil and food antioxidant additives, but also cosmetics in the anti-ultraviolet inhibitors, has been large-scale application and industrial production. As a natural product, the phenolic hydroxyl groups in the polyphenols plant represented by PG are easy to complex with the metal ions, and the coordination is formed to form a relatively stable organometallic complex. The copper ion binding energy of the gallate and the cancer cells Effectively inhibit cancer cells, blocking its cell synthesis.

Gallate compounds are important derivatives of gallic acid and are also a safe synthetic antioxidant. The antioxidant activity of oil is stronger than that of BHT (2,6-di-tert-butyl-p-cresol) and BHA

(Tert-butylhydroxyanisole), while the bacteria, yeast and mold have a strong inhibitory effect, it is a multi-functional food antioxidants. Gallates have a strong scavenging effect on free radicals in the human body, with the function of anti-aging, prevention of cardiovascular disease[19-23] one of the amyl amylate in addition to the treatment of cardiovascular and cerebrovascular diseases. Free radicals, the inflammation, viral diseases, radiation damage, allergies and aging have a certain effect; is also a fat-soluble antioxidant, chemical, light industry, medicine, food and other industries have a wide range of use used as a food antioxidant, a new type of photosensitive material additives and in toothpaste as an antibacterial agent to inhibit dental caries[24,25]. At present, the research on gallic acid mainly concentrates on the verification and quantitative detection of the antioxidant mechanism of various natural product extracts, and the related research reports are more, but the metal complexes are reported less.

2. Materials and methods

2.1. Experimental apparatus and reagents

Infrared spectrometer, electrochemical workstation and its attached three-electrode system, electric stirrer, condensate reflux water separator, thermometer, three-flask.

Gallate, $CuCl_2$, NaOH, saturated KCl solution, double distilled water, isoamyl alcohol, phosphotungstic acid, activated carbon benzene, ethanol. (All reagents are of analytical grade)

2.2 Experimental steps

2.2.1 Preparation of isoamyl gallate

The synthesis of gallate is based on a certain amount of gallic acid and the corresponding alcohol, under the action of the catalyst reflux reaction. The basic reaction principle shown in **Figure 3**:

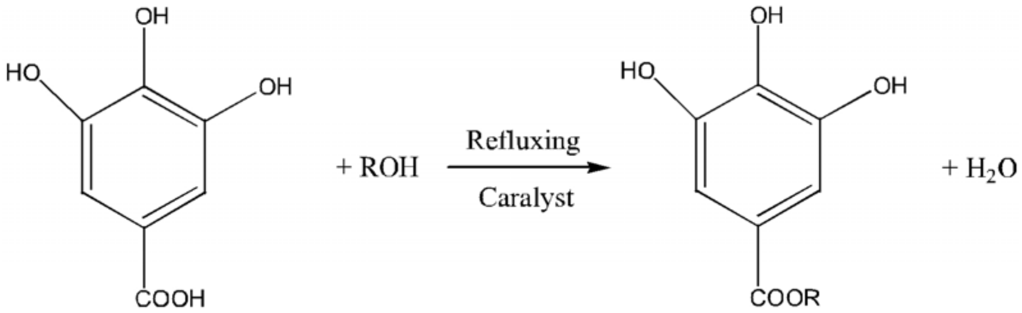

Figure 3. Synthesis of gallate.

The esterification reaction is a reversible reaction, and the reverse reaction is the hydrolysis of the ester. The esterification reaction can be carried out according to the different mechanism depending on the structure of the carboxylic acid and the alcohol and the reaction conditions. Esterification, the dehydration between carboxylic acid and alcohol can be two different ways, as shown in **Figure 4**:

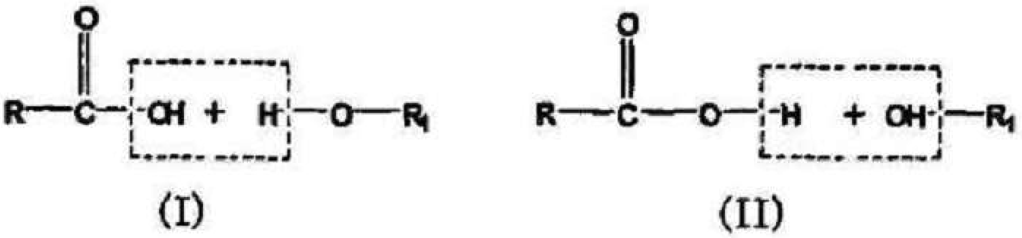

Figure 4. Carboxylic acid and alcohol dehydration in two ways. (I) is a combination of a hydroxyl group in a carboxylic acid and hydrogen in an alcohol to form a water molecule, and the remainder is bound to an ester. Since the carboxylic acid molecule removes the hydroxyl group and the remainder is the acyl group, the mode (I) is referred to as the acyloxy bond breakage. (II) is composed of hydrogen and alcohol in the carboxylic acid to form water, and the remainder is bound to the ester. Since the alcohol is removed after removal of the hydroxyl group, the scheme (II) is referred to as an alkoxy bond breakage.

Experiments show that majority of carboxylic acid and alcohol esterification reaction is carried out according to the formula (I).

According to the above basic principles and mechanism of reaction, synthesis of isoamyl gallate: activated carbon immobilized phosphotungstic acid as a catalyst[24], synthetic gallic acid, isoamyl ester, the yield of more than 95%.

2.2.1.1 Preparation of supported catalyst

Weigh a certain amount of activated carbon, add to a certain concentration of phosphotungstic acid aqueous solution, heated reflux 3 h, placed overnight, pouring liquid, washed to neutral, dried at 100 °C 3 h, then dried at 120 °C to constant weight to obtain activated carbon immobilized phosphotungstic acid. By controlling the concentration of phosphotungstic acid and the time of loading, different supported catalysts can be obtained. The amount of catalyst supported is calculated by increasing the amount of activated carbon before or after the adsorption or the reduction of phosphotungstic acid.

2.2.1.2 Synthesis of isoamyl gallate

(9.4 g), benzene, and quantitative isoamyl alcohol and catalyst were added in a three-necked flask (100 mL) equipped with an electric stirrer, a condensate reflux separator and a thermometer, and the temperature was gradually heated, the temperature was raised, and the reaction was controlled When the temperature is between 105 and 110 °C, the reaction is stopped for a certain period of time, and the catalyst is removed by filtration, and the excess amount of isoamyl alcohol and the water-carrying agent (distillation treatment) are distilled off by steam distillation. The reaction into a certain amount of cold water, precipitation of a large number of white precipitate, until the product completely precipitated, decompression pumping, the product. Vacuum drying, weighing, measuring the melting point, calculate the yield.

2.2.2 Preparation of copper complexes of isoamyl gallate

Preparation of isopentyl gallate copper complex according to[26] Weigh 0.55763 g (0.00232 mol) isoamyl gallate, 0.1015 g (0.2538 mol) NaOH, 0.1520 g (0.00113 mol) $CuCl_2$. The isoamyl gallate was dissolved in hot water at 40 °C, stirred, added with NaOH and CuCl2 aqueous solution, red brown precipitate was produced and stirring was continued for 4.0 h[27,28]. Filtration, washing and drying, that was complex, the yield of 15%.

2.2.3 Pretreatment of electrodes

Glassy Carbon Electrode: The glassy carbon electrode (2 mm) was polished to the mirror on the suede before the experiment. After each polishing, the mixture was heated in a boiling water bath for 5 minutes with a concentrated sulfuric acid hydrogen peroxide mixed solution (3:1) Ultrasonic ultrasound for 1 minute. Before each experiment, the glassy carbon electrode was subjected to cyclic voltammetry in a 1 $mol \cdot L^{-1}$ sulfuric acid solution with a scanning rate of 50 $mV \cdot s^{-1}$ and a scanning potential of -1.0-1.0 V Scan to reach a stable cyclic voltammetry curve.

Electrode: The platinum electrode used for the test was the counter electrode, and the ultrasound was performed in ethanol for 1 minute before the experiment.

Reference electrode: experimental calomel electrode as the reference electrode, before the experiment in the double distilled water ultrasound.

3. Results and discussion

3.1. Infrared spectroscopy analysis

The IR spectra of IG and IG-Cu in the range of 250~4000 cm^{-1} are shown in **Figure 5** and **Figure 6**, respectively.

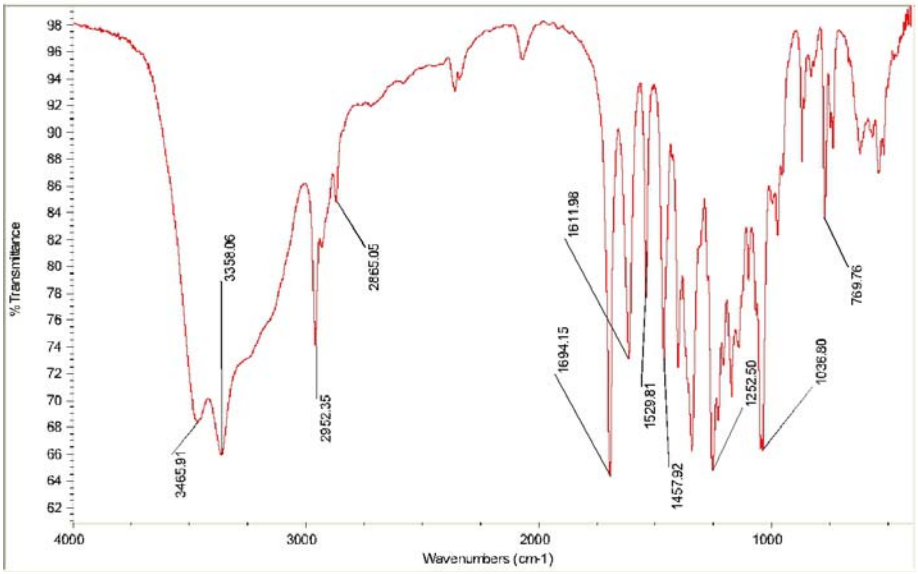

Figure 5. Infrared spectra of isoamyl gallate.

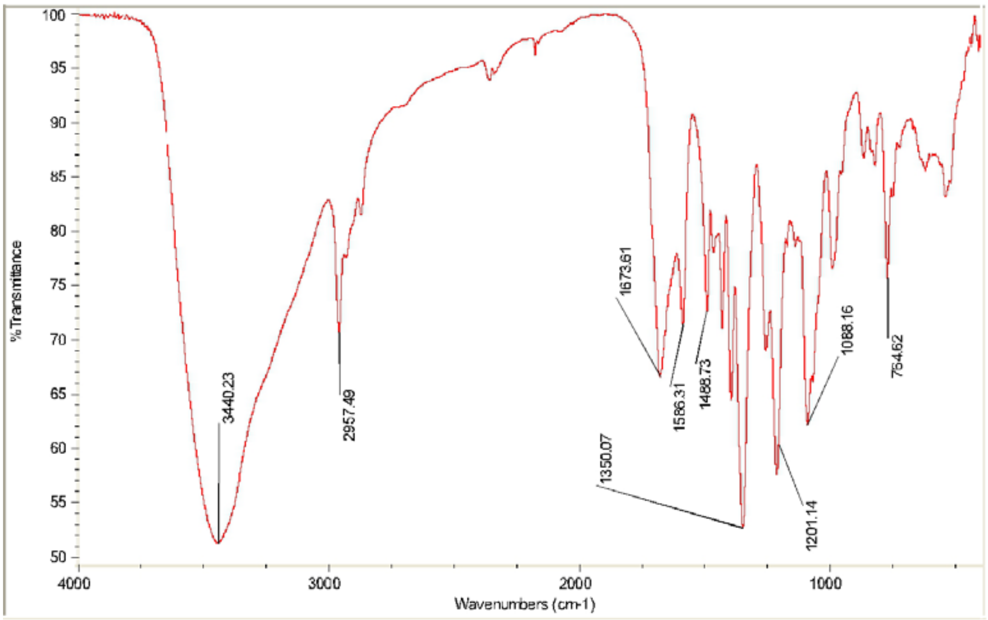

Figure 6. Infrared spectra of isocyanate copper metal complex.

As shown in the figure, the infrared spectrum of gallate isoamyl ester has undergone significant es before and after the formation of the complex. These changes are due to metal coordination. There are two obvious absorption peaks of phenolic hydroxyl stretching in the vicinity of 3,400~3,500 cm^{-1}, while in the infrared of the complex IG-Cu, the two chemical environments are different. The phenolic hydroxyl group is only one compound after cleavage, which is consistent with the literature reported, and the presence of crystalline water is reported here in the literature according to the literature. In addition, the peaks of the phenolic hydroxyl groups in the vicinity of 1,300 cm^{-1} also shifted blue, which also confirmed that the oxygen atoms on the phenolic hydroxyl groups were involved in the coordination of metals.

The absorption peaks of the benzene ring in the ligand were 1,618 cm^{-1}, 1,538 cm^{-1} and 1,468 cm^{-1}, and moved to 1,585 cm^{-1}, 1,491 cm^{-1} and 1430 cm^{-1} in the complex. The red shift of the C=C absorption peak indicates that the oxygen on the benzene ring is coordinated with the metal ion and passed to the C=C by the conjugation effect so that the strength of the C=C bond decreases. It also shows that after the formation of complexes, there is a greater electron transfer. The νC=O absorption peak of the ligand ester group was 1,693 cm^{-1} and shifted to 1,680 cm^{-1} after coordination. The absorption peak did not move significantly, indicating that the ester group did not participate in the coordination. A new peak appears near 600 cm^{-1}, which is the absorption peak of Cu-O bond.

3.2. Electrochemical analysis

In the experiment to take nafion attached to the electrode surface of the method, the solid IG-Cu dissolved in water, with a gun to take 1ml drops on the glass carbon electrode, until the water evaporates again, and then drop nafion. In the experiment, the three electrode system was used, the glassy carbon was used as the working electrode, the platinum plate was the counter electrode, the saturated calomel electrode was the reference electrode, and the saturated potassium chloride solution was the electrolyte solution.

IG and IG-Cu cyclic voltammetry curves are shown in **Figure 7** and **Figure 8**, respectively. The results of cyclic voltammetry are shown in **Table 1**.

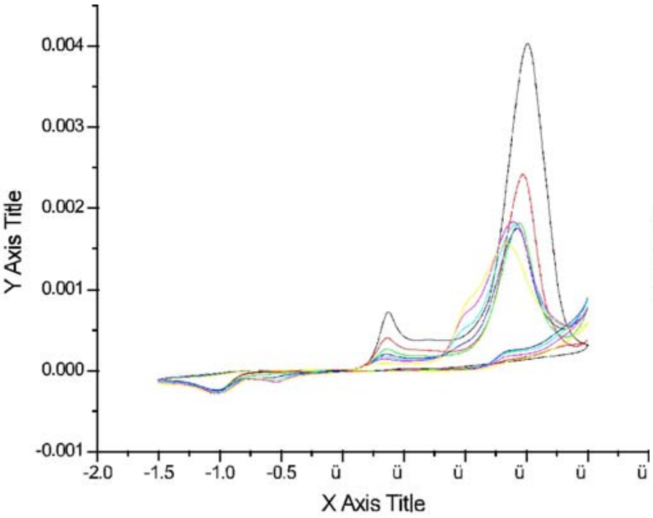

Figure 7. IG cyclic voltammetry curve.

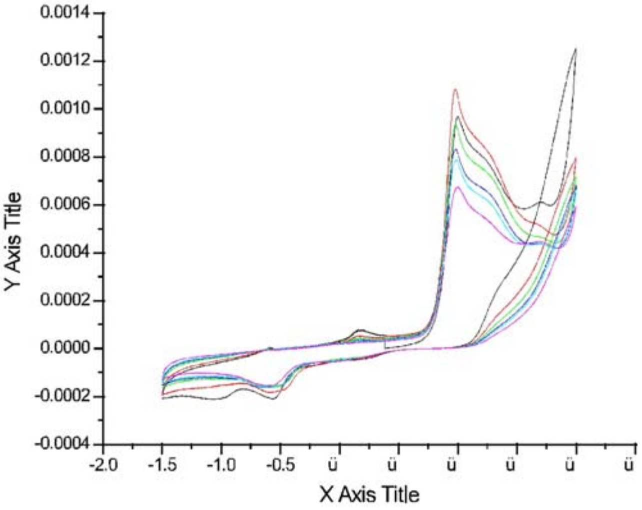

Figure 8. IG-Cu cyclic voltammetry curve.

Compound	oxidation peak Ep, a/V		reduction peak Ep, c/V		E1/2/V	
	(1)	(2)	(1)	(2)	(1)	(2)
IG		1.309		0.190		0.235
IG-Cu	0.158	0.542	-0.428	-0.0502	-0.399	0.015

Table 1. Cyclic voltammetry parameters

From the table, we can see that the electrochemical properties of IG before and after coordination were significantly changed. IG between -1.0~2.0 V only a pair of redox peaks, benzene ring for the three phenolic hydroxyl redox produced[29], IG-Cu in -1.0~2.0 V between the two pairs of redox peaks, respectively Corresponding to CuI/CuII electricity pairs and CuII/CuIII pairs[30,31]. The half-wave potential of IG-Cu is smaller than IG, indicating that after the coordination of metal, the conjugated system increases, the electron cloud density decreases, the degree of electron delocalization in the whole molecule is higher than that of IG and Cu. Large, easier to lose electrons, and thus have a high redox activity[32].

Cyclic voltammetry curves show that the coordination peak potential and the reduction peak potential are obviously reduced, but the reversibility is enhanced, indicating that the metal complex is more easily oxidized and difficult to be reduced. Souza *et al.*[33] reported that the antioxidant strengths and weaknesses of polyphenols and their complexes, such as flavonoids, were obtained from the cyclic voltammetric peak potential, the better the oxidation resistance was. Therefore, the oxidation resistance of IG-Cu is better than that of IG ligand.

4. Conclusions

Infrared spectra show that the structure of the gallate isoamyl ester has changed significantly due to the coordination of the metal. Two of the chemical environment of different phenolic hydroxyl groups after complexing only one, confirmed that the oxygen on the phenolic hydroxyl atoms involved in the coordination of the metal.

By cyclic voltammetry, it is found that the half-wave potential of IG-Cu is smaller than IG, indicating that after the coordination of metal, the conjugation system increases, the electron cloud density decreases, the electrons in the whole molecule are larger and easier to lose Electrons, and thus have a high redox activity, therefore, IG-Cu oxidation resistance is better than IG ligand.

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Conflict of interest

The authors declare no potential conflicts of interest.

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