Study on Coordination Properties of Metal Ions-Flavonoid Compound

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Abstract. The coordination ratio of rutin and Cu\textsuperscript{2+} was studied. And its coordination mechanism was discussed, which provided a basis for the preparation of rutin-metal complex. Ultraviolet spectrophotometry was used to determine the coordination condition. Constant mole continuous change method, varying concentration method and infrared spectroscopy were used to determine the composition and structure of the complex respectively. The results shown that the best coordination ratio of rutin with Cu\textsuperscript{2+} was Cu (II): Ru=1:2.

1. Introduction

Rutin (Ru) belongs to polyhydroxy flavonoids and has the same pharmacological activities as vitamin P. It can reduce vascular brittleness and abnormal permeability [1]. Ru was used as auxiliary therapeutic agent to prevent hypertension and arteriosclerosis [2]. With obvious coronary artery dilation function Ru has been used to treat coronary heart disease in the clinical [3]. It also has anti-inflammatory effects [4]. It can coordinate with many metals for spectrophotometric, polarographic, fluorescence and chemiluminescence analysis [5].

The coordination theory of Traditional Chinese Medicine (TCM) think that the effective components of TCM were mainly coordination compounds composed of organic molecules and trace elements. Compared with pure organic molecules and trace elements, coordination compounds more comprehensively reflect the material basis of TCM. And they represent the active centre of TCM. For example, Ru itself does not kill cancer cells, CuSO\textsubscript{4} solution also has only a slight killing power against cancer cells, but coordination compound of Cu (II)-Ru has a greater effect on killing cancer cells [6].

Free radicals are intermediate products of biochemical reaction of human life activities. Under normal circumstances, the production and elimination of free radicals in the body are in dynamic equilibrium. But if they were produced too much or cleared too slow, which may cause damage to body at molecular level, cellular level and organic level. They can attack carbohydrate, protein, fat, nucleic acid and so on to accelerate the aging process of the body, or induce cancer, cardiovascular disease and many other diseases. And Ru has the properties of scavenging free radicals [7].

The results shown that the properties of antibacterial and antioxidant of metal ions-flavonoid compound was changed significantly [8]. Ultraviolet spectrophotometry used to determine the coordination conditions, coordination ratio and coordination constant of Ru-Cu (II). And their
coordination mechanism was discussed, which provided certain theoretical basis for the development of coordination type of Chinese herbal medicine and the study of pharmacological effects.

2. Materials

2.1. Chemicals and reagents
Drugs and reagents Ru (purity of 95%) was supplied by Shanghai spectral instrument co. LTD. Absolute ethyl alcohol and CuSO₄·5H₂O were supplied by Tianjin fengchuan chemical reagent co. LTD. Sodium hydroxide, acetic acid and sodium acetate were all bought from Tianjin north tianyi chemical reagent factory. Sodium dihydrogen phosphate was supplied by Tianjin fine chemical industry research institute.

2.2. Instruments
SP-2102 ultraviolet visible spectrophotometer was provided by Shanghai spectrum instruments co., LTD. Bio-rad FTS 6000 Fourier transform infrared spectrometer was supplied by American Bio-rad Company. Magnetic stirring apparatus was purchased from Germany WIGGENHAUSER group. QL-901 vortex mixer was provided by Jiangsu haimen qilinbeier instrument manufacturing co., LTD. FA1004 analytical balance was supplied by Shanghai balance instrument factory. Perkin Elmer-spectrum10 infrared spectrometer (platinum Elmer companies in the United States).

3. Method

3.1. Ultraviolet-visible spectroscopy of Ru-Cu (II) complexes
2mL Ru standard, 0.5 mL CuSO₄ and 2mL HAc-NH₄Ac solution was diluted with water to 10 mL. Then the solution was used to scale for UV visible full-wavelength scanning (200-800nm), and the corresponding solution without metal ions was used as reference. The maximum absorption wavelength and absorbance of the complex were recorded.

3.2. Determination of complex composition
3.2.1. Variable concentration method. 2mL HAc-NH₄Ac and 0.6mL Cu (II) standard solution were added to a 10 mL volumetric flask. Then 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 mL Ru standard solution was added to the volumetric flask respectively. And the corresponding solution was used as reference. The absorbance of the complex was determined at 398 nm.

3.2.2. Iso-molar continuous variation method. 2mL HAc-NH₄Ac and 1.5 mL Ru-Cu (II) solution were added to a 10 mL volumetric flask. The amount of Ru-Cu (II) solution was fixed as 1.5 mL. And the volumes of Ru and Cu (II) were keeping changing respectively which were added to the volumetric flask. And the corresponding solution was used as reference. The absorbance of the complex was determined at 398 nm.

3.3. Fourier transforms infrared spectroscopy of Ru-Cu (II) complex
The obtained complexes were fully dried and then scanned by infrared spectroscopy. That was used to determine the main functional groups of Ru and Ru-Cu (II) complex.

4. Results and discussion

4.1. Ultraviolet-visible spectroscopy of Ru-Cu (II) complex
Ultraviolet-visible spectroscopy of Ru-Cu (II) complex result was shown in Figure 1. The maximum absorption wavelength of Ru is 375 nm. And the result showed that the maximum absorption wavelength of the Ru-Cu (II) complex was 398 nm, which red shifted 23 nm. This shown that the complex was formed.
4.2. Determination of complex composition

4.2.1. Variable concentration method. The absorbance of the complex changing with the concentration of Ru was shown in Figure 2. The result showed that the turning point occurred around 1.00 mL. This shown that the ratio of the complex was Cu (II): Ru = 1: 2.
4.2.2. Iso-molar continuous variation method. The absorbance of the complex changing with the concentration of Ru was shown in Figure 3. The result showed that the turning point occurred to the range of 0.9-1.00 mL meaning that the volume ratio of Cu (II) and Ru is 1:2. This shown that the ratio of the complex was Cu (II): Ru = 1:2.

4.3. Fourier transforms infrared spectroscopy of metal complexes
The infrared spectroscopy of Ru-Cu (II) and Ru standard were shown in Figure 4 and 5, respectively. The complexes shown characteristic peaks of carboxyl, phenol hydroxyl and ether oxygen radicals, and the absorption peaks of the complex were significantly different from those of ligand. The wide peak of ligand and complex at 3400cm⁻¹ was the stretching vibration absorption peak of coordination water, alcohol and phenol light groups. Ligand molecule has multiple hydroxyl groups which resulted complex have no effect on the peak. The stretching vibration absorption peak of the ligand appeared at 1655cm⁻¹, and the coordination weakened the C=O bond, so the corresponding absorption peak moved to the low-wave-number region. So in the complex, the peak overlapped with the absorption peak of benzene ring at 1610cm⁻¹, indicating that the group participated in coordination reaction. The two peaks of ligand at 1600cm⁻¹ and 1500cm⁻¹ were the stretching vibration absorption peaks of C=C bond of benzene ring conjugate system. And these two peaks were basically kept in the original position in the complex, indicating that the coordination reaction had little influence on the benzene ring conjugate system. The two spectral peaks of ligand at 1360cm⁻¹ and 1290cm⁻¹ were the stretching vibration of phenol through C-O bond and the deformation vibration coupling of O-H bond. Both of which were shifted to lower wave number region and appeared at 1350cm⁻¹ and 1275cm⁻¹, indicating that phenol light group was involved in coordination bonding. The absorption peak of ligand at 1200cm⁻¹ was the C-O-C stretching vibration absorption peak of ether, which only slightly shifted to the high-wave-number region, which excluded the possibility of ether oxygen atoms forming bonds. The M-O bond stretching vibration absorption peak was observed at 634cm⁻¹, indicating that Ru and Cu²⁺ were interacted to form complex.
5. Conclusion
The optimum reaction ratio of Cu (II): Ru complex was obtained by experiments, Cu (II): Ru=1: 2. And the possible structure of the complex was analyzed by ultraviolet and infrared spectroscopy. It provides a basis for the preparation of Ru-metal complex.

Figure 4. The infrared spectroscopy of Ru-Cu (II)

Figure 5. The infrared spectroscopy of Ru standard
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