Synthesis and characterization of coordination compounds of Cd(II), Co(II), Ni(II), Cu(II) and Zn(II) with rutin

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The synthesis, characterization and electrochemical properties of five novel coordination compounds of rutin with transition metal [M = Cd(II), Co(II), Ni(II), Cu(II) and Zn(II)] are reported here. These coordination compounds may be formulated as [M3L2(H2O)n(CH3COO)(n=6,12)]. Three hydroxy groups on the unsaturated rings form coordination bonds with the metal ions. The cyclic voltammetric data show changes in the redox potentials and currents of the coordination compounds relative to that of rutin. Formation of the coordination compounds changes the rigidity of rutin molecular plane and has a little influence on the antioxidation of rutin.

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Flavonoids, found widely in fruits, vegetables, legumes, nuts and seeds of vascular plants, are always considered as antioxidants, antiinflammatory, antimicrobial, anticancer, etc., and utilized widely in pharmaceutical industry.

Flavonoids have strong ability to coordinate with metal ions. In recent years, research interests on flavonoids and their corresponding metal coordination compounds have increased. It is considered that bioactivity of coordination compounds of metal ions with flavonoids is related to their corresponding structure and interaction between the flavonoids and the metal ions may change the antioxidant properties and some biological effects of the host molecules.

Also, it is suggested that the bioactivity of an organic ligand may be increased when coordinated to suitable metal ions.

Flavonoids are derivatives of benzo-γ-pyrones with two aromatic rings (Rings A and B, Fig. 1) linked through three carbons that usually form an oxygenated heterocycle (C ring, Fig. 1). Investigations on solid coordination compounds of rutin (H3L) are seldom reported. Recently, we have reported the electrochemical investigation of rutin, quercetin, morin and their Eu(III) and Zn(II) coordination compounds and the interaction with DNA. In order to investigate the interaction of flavonoids with metal ions, herein we report the synthesis, characterization and electrochemical investigation of five novel coordination compounds of rutin with Cd(II), Co(II), Ni(II), Cu(II) and Zn(II). Elemental analysis, ICP, molar conductivity, UV-Vis, IR, 1H NMR, fluorescence spectroscopy and electrochemistry have been used to characterize these coordination compounds.

Materials and Methods
All reagents and solvents were of analar grade. Rutin was purchased from Sigma Co. EtONa was prepared with small, freshly cut pieces of Na (1.15 g) added to dry EtOH (50 cm3).

Elemental analyses were performed using PE-2400 CHN instrument. Cd(II), Co(II), Ni(II), Cu(II) and Zn(II) were determined with a model ARL 3520 ICP-AES, inductively coupled plasma atomic emission spectrometer. Molar conductance at room temperature was measured in 10-3 M H2O solution using a DSS-

Fig. 1 — The structure of rutin.
11A type conductivity meter. IR spectral data in the 600-4000 cm\(^{-1}\) range were recorded on a Nicolet NEXUS 670 FT-IR spectrometer using KBr pellets. \(^{1}H\) NMR spectra were obtained on an Advance Varian Mercury-400 spectrometer. UV-vis spectra, in H\(_2\)O, were recorded on an Agilent 8453 using standard 1.00 cm quartz cell. The fluorescence spectra were recorded on a Shimadzu spectrofluorimeter using a quartz cells. The cyclic voltammograms were equipped with a glassy carbon-working electrode, a reference electrode in platinum wire auxiliary electrode and a Ag/AgCl electrode, rutin (I mmol) and absolute EtOH (70 cm\(^3\)) were placed. The mixture was cooled to room temperature and the separated solid was filtered, washed with EtOH and H\(_2\)O three times. The solid product was dried in air.

The metal coordination compounds were prepared as already reported\(^5\). In a 200 cm\(^3\) three-necked, round-bottomed flask provided with an electromagnetic stirrer and reflux condenser, rutin (1 mmol) and absolute EtOH (70 cm\(^3\)) were placed. The flask was then heated on an oil-bath. After the above reagents dissolved, EtONa solution (0.5 cm\(^3\)) was added, followed by metal acetate (1 mmol) and the solution was heated to reflux for 6 h while stirring. The mixture was cooled to room temperature and the separated solid was filtered, washed with EtOH and H\(_2\)O three times. The solid product was dried in air.

Results and Discussion

The coordination compounds are soluble in DMSO, and slightly soluble in EtOH, MeOH and H\(_2\)O, but scarcely soluble in CHCl\(_3\) and CH\(_2\)Cl\(_2\). Table 1 shows the molar conductance and elemental analysis data that suggest that the ratio of metal ion and rutin is 3:2 in the coordination compounds. The molar conductivity data show that there are CH\(_3\)COO anions outside the coordination sphere.

IR spectra

IR spectral data of rutin and the coordination compounds prove that the coordination compounds are formed indeed by the reactions between the transition metals and rutin. The broad bands at 3391-3434 cm\(^{-1}\) indicate the existence of water molecules in the coordination compounds, and the shifting of these bands relative to rutin suggests that the –OH on the unsaturated rings of rutin participates in the coordination with metal ions. The strong absorption bands at 1656-1650 cm\(^{-1}\) of C=O of the coordination compounds show that the carbonyl O atom does not participate in coordination. As compared to rutin, the absorption bands of benzene ring and C-O-C do not shift, showing thereby, that the O atom of C ring (position 1, Fig. 1) is not involved in the coordination. The bands for v(M-O) in 636-609 cm\(^{-1}\), which were not observed in the IR spectrum of rutin, indicate the formation of coordination bands between rutin and metal ions\(^13\).

\(^{1}H\) NMR spectra

Table 2 shows the \(^{1}H\) NMR data of rutin and the corresponding coordination compounds. The proton signals due to –OH on the unsaturated rings of rutin in the low field are observed in the coordination compounds. These data indicate that the protons of 7-OH and 3'-OH of rutin are displaced from the ligand, and O atoms participate in the coordination with metal ions, but 5-OH and 4'-OH do not participate in the coordination reaction because of their low proton acidity. The other proton signals of benzene ring of the coordination compounds are shifted to higher field relative to rutin. This is probably due to the increase of conjugation caused by coordination when the coordination compounds are formed.

UV-vis spectra

UV-vis spectra have long been used for the structural analysis of flavonoids. The typical
observed due to the polarity of the solvent and the absorption peak of the electronic rings A and B indicate that rings A and B are involved in strong solvent-solute interactions. The change of wavelength and intensity of the absorption peaks of rings A and B correspond to the B-ring wavelength and intensity of the absorption peaks of bonds are probably hindered by the former ones. The bands have been predicted to the absorption in the range 256-267 nm is due to the A-ring portion, and the specific and useful for obtaining information regarding identification. The position and relative intensities of these maxima may yield information on the coordination with metal ions.

UV-vis spectra are shown in Fig. 2 and Table 3. Rutin exhibits three major absorption bands in the ultraviolet/visible range (Fig. 2). The absorption in the range 256-267 nm is due to the A-ring portion, and the absorption in the range 352-402 nm corresponds to the B-ring portionThese absorption bands have been predicted to arise from \( \pi \rightarrow \pi^* \) electronic transitions and are highly absorptive. The absorption peak of the \( \pi \rightarrow \pi^* \) transition of the \( \text{C}=\text{O} \) bond is probably hindered by the former ones. The fine vibrational structure of the spectrum is obscured due to the polarity of the solvent and the strong solvent-solute interactions. The change of wavelength and intensity of the absorption peaks of rings A and B indicate that rings A and B are involved in the coordination reaction and the metal-oxygen band is formed. In comparison with the rutin absorption spectra, the wavelength of the coordination compounds is changed to long-wavelength region.

### Table 2 — \(^1\)H NMR spectra data of rutin and the coordination compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(^1)H NMR ((\delta), ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutin</td>
<td>12.64(s, 1H, 5-OH), 10.83(s, 1H, 7-OH), 9.67(s, 1H, 4'-OH), 9.18(s, 1H, 3'-OH), 7.56(d, 1H, 2'-H), 7.52(d, 1H, 5'-H), 6.84(d, 1H, 6'-H), 6.38(d, 1H, 8-H), 6.19(d, 1H, 6-H)</td>
</tr>
<tr>
<td>([\text{Cd}(_2\text{L})_2\text{H}_2\text{O}_6]\text{CH}_3\text{COO}_2)</td>
<td>12.59(s, 1H, 5-OH), 9.50(s, 1H, 4'-OH), 7.52(d, 1H, 2'-H), 7.38(d, 1H, 5'-H), 6.64(d, 1H, 6'-H), 6.22(d, 1H, 8-H), 6.02(d, 1H, 6-H)</td>
</tr>
<tr>
<td>([\text{Co}(_2\text{L})_2\text{H}_2\text{O}_6]\text{CH}_3\text{COO}_2)</td>
<td>12.43(s, 1H, 5-OH), 9.59(s, 1H, 4'-OH), 7.55(d, 1H, 2'-H), 7.49(d, 1H, 5'-H), 6.50(d, 1H, 6'-H), 6.19(d, 1H, 8-H), 5.93(d, 1H, 6-H)</td>
</tr>
<tr>
<td>([\text{Ni}(_2\text{L})_2\text{H}_2\text{O}_6]\text{CH}_3\text{COO}_2)</td>
<td>12.49(s, 1H, 5-OH), 9.53(s, 1H, 4'-OH), 7.54(d, 1H, 2'-H), 7.51(d, 1H, 5'-H), 6.78(d, 1H, 6'-H), 6.27(d, 1H, 8-H), 5.87(d, 1H, 6-H)</td>
</tr>
<tr>
<td>([\text{Cu}(_2\text{L})_2\text{H}_2\text{O}_6]\text{CH}_3\text{COO}_2)</td>
<td>12.52(s, 1H, 5-OH), 9.55(s, 1H, 4'-OH), 7.50(d, 1H, 2'-H), 7.21(d, 1H, 5'-H), 6.80(d, 1H, 6'-H), 6.07(d, 1H, 8-H), 5.98(d, 1H, 6-H)</td>
</tr>
<tr>
<td>([\text{Zn}(_2\text{L})_2\text{H}_2\text{O}_6]\text{CH}_3\text{COO}_2)</td>
<td>12.59(s, 1H, 5-OH), 9.55(s, 1H, 4'-OH), 7.52(d, 1H, 2'-H), 6.82(d, 1H, 5'-H), 6.35(d, 1H, 6'-H), 6.13(d, 1H, 8-H), 5.96(d, 1H, 6-H)</td>
</tr>
</tbody>
</table>

### Table 3 — UV-vis and fluorescence data of rutin and the coordination compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV-vis (\lambda_{\text{max}}) (nm), (e) in (M^{-1}\text{cm}^{-1})</th>
<th>Fluorescence, (Excitation wavelength: 306 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutin</td>
<td>204 Band I 256 Band II 352</td>
<td>Emission wavelength (nm) Relative fluorescence intensity</td>
</tr>
<tr>
<td>([\text{Cd}(_2\text{L})_2\text{H}_2\text{O}_6]\text{CH}_3\text{COO}_2)</td>
<td>204 265 358</td>
<td>418.6 20.7</td>
</tr>
<tr>
<td>([\text{Co}(_2\text{L})_2\text{H}_2\text{O}_6]\text{CH}_3\text{COO}_2)</td>
<td>204 262 356</td>
<td>458.1 37.5</td>
</tr>
<tr>
<td>([\text{Ni}(_2\text{L})_2\text{H}_2\text{O}_6]\text{CH}_3\text{COO}_2)</td>
<td>204 262 356</td>
<td>451.2 10.2</td>
</tr>
<tr>
<td>([\text{Cu}(_2\text{L})_2\text{H}_2\text{O}_6]\text{CH}_3\text{COO}_2)</td>
<td>209 267 402</td>
<td>425.6 19.8</td>
</tr>
<tr>
<td>([\text{Zn}(_2\text{L})_2\text{H}_2\text{O}_6]\text{CH}_3\text{COO}_2)</td>
<td>204 265 360</td>
<td>453.5 25.3</td>
</tr>
</tbody>
</table>

Flavonoid spectrum consists of two maxima in the range of 240-285 nm determined by the A ring, and at 300-550 nm determined by B ring, which is more specific and useful for obtaining information regarding identification. The position and relative intensities of these maxima may yield information on the coordination with metal ions.

![UV-vis spectra of rutin and the coordination compounds](image-url)
and such bathochromic shift is related to the extension of the conjugated system with the coordination effect.

There is also another absorption band of the rutin coordination compounds observed in the 204-209 nm range corresponding to benzene ring structure in rutin. Comparing with rutin, the $E_2$ absorption bands of the coordination compounds are not changed except copper coordination compound, of which the absorption bands I and II also have a bigger red shift compared with the others. This is attributed to the fact that the copper coordination compound readily forms planar molecular structure and hence conjugation is stronger than the others, leading to a bigger bathochromic shift relative to the others. This phenomenon is also observed earlier, as reported by Zhang et al., where the wavelength of UV-vis absorption of band II of copper coordination compound is higher than the other transition metal coordination compounds.

**Fluorescence spectroscopy**

The fluorescence data of rutin and the coordination compounds are listed in Fig. 3 and Table 3. The fluorescence data show that rutin itself exhibits a strong fluorescence. The emission wavelength of all the coordination compounds shifts to longer wavelengths (7-40 nm) relative to rutin under the same excitation wavelength. The red shift of emission wavelength is related to the change of the energy level difference of the highest occupied molecular orbital and the lowest unoccupied orbital of rutin. The change of fluorescence intensity of the coordination compounds is attributed to the coordination effect, which changes the rigidity of rutin structure and promotes the fluorescence quantum yield by reducing the probability of non-radiative energy dissipation process.

**Electrochemical properties of the coordination compounds**

The cyclic voltammograms of 5.0x10⁻³ M rutin have a pair of reversible redox peaks at 0.407 V ($E_{pc}$) and 0.370 V ($E_{pa}$) respectively, with $\Delta E$ ($E_{pc}-E_{pa}$) = 37 mV in the 0.1 M HAc-NaAc (pH=5.22) buffer solution for bare glass carbon electrode (Table 4). Rutin is oxidized in electrolysis with a two-electron process...
forming quinone compounds. Fig. 4 shows the cyclic voltammetric curve of free ligand and the coordination compound of Cd(II).

The cyclic voltammetric data show that there is a positive shift of the oxidation potentials and a decrease of the oxidation current of the coordination compounds relative to those of rutin, and this change suggests the formation of coordination compounds. Giovani et al. have reported that there is a relationship between the antioxidant activity and the cyclic voltammetric oxidation peak potential for flavonoids and coordination compounds. The observed change of potential value ($E_{pa}$ and $E_{pc}$) of the metal coordination compounds in the range of 4-26 mV is less relative to that of rutin. Thus, coordination reactions of rutin with Cd(II), Co(II), Ni(II), Cu(II) and Zn(II) etc. have a little influence on the antioxidant activity of rutin.

According to the previous literature, and the above experimental data, the postulated structure of the coordination compounds of rutin with transition metal ions is shown in Fig. 5.

**Acknowledgment**

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**References**