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Solid complexes of iron(II) and iron(III) with rutin

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Abstract Solid complex compounds of Fe(II) and Fe(III) ions with rutin were obtained. On the basis of the elementary analysis and thermogravimetric investigation, the following composition of the compounds was determined: (**1**) $FeOH(C_{27}H_{29}O_{16})\cdot 5H_2O$, (**2**) $Fe_2OH(C_{27}H_{27}O_{16})\cdot 9H_2O$, (**3**) $Fe(OH)_2(C_{27}H_{29}O_{16})\cdot 8H_2O$, (**4**) $[Fe_6(OH)_2(4H_2O)(C_{15}H_7O_{12})SO_4]\cdot 10H_2O$. The coordination site in a rutin molecule was established on the basis of spectroscopic data (UV–Vis and IR). It was supposed that rutin was bound to the iron ions via 4C=O and 5C—oxygen in the case of (**1**) and (**3**). Groups 5C–OH and 4C=O as well as 3′C–OH and 4′C–OH of the ligand participate in binding metals ions in the case of (**2**). At an excess of iron(III) ions with regard to rutin under the synthesis conditions of (**4**), a side reaction of ligand oxidation occurs. In this compound, the ligands' role plays a quinone which arose after rutin oxidation and the substitution of Fe(II) and Fe(III) ions takes place in 4C=O, 5C–OH as well as 4′C–OH, 3′C–OH ligands groups. The magnetic measurements indicated that (**1**) and (**3**) are high-spin complexes.

Keywords Iron · Rutin ·
Spectroscopic and magnetic properties

Introduction

Flavonoids are a group of compounds characterized by diverse structure and various biological activities. In the nature, they are widespread as glycosides and in this form are well absorbed by the body organisms. Bioflavonoids used to be called vitamin P. In fresh plants, rutin occurs frequently with vitamin C because it has similar properties to vitamin C; these substances well complement one another. In health care, a specimen including both compounds is administered. Rutin increases flexibility and tightness of capillaries, which efficacious that the vessels keep the plasma proteins out—these proteins are often responsible for skin inflammatory and allergy [1].

In recent years, hydroxyflavones have been intensively determined for the sake of their antioxidant properties [2–9]. In [5], it was stated that flavonoids, which are capable of binding metal ions, are less susceptible to oxidation than free compounds.

Flavonoids' complex and redox properties are connected with hydroxyl group position in a molecule. In rutin molecule (5,7,3′,4′-tetrahydroxyflurone-3-*β*-D-rutinoside), the following coordination sites of metal ions are possible (Fig. 1).

Iron as a hemoglobin component plays an important biological role in human organism. However, iron excess is harmful because of the increase in oxidation stress and formation of reactive oxygen species, which efficacious lipid, protein, and nucleic acids oxidation [10].

Chelation (especially iron) potency among other things rutin and radical scavenging activities of flavonoids are most useful for inhibition of lipid peroxidation description [6, 7].

van Acker et al. [8] stated that the scavenger potencies of flavonoid (rutin) metal (Cu^{2+}, Fe^{2+}, and Fe^{3+}) complexes were significantly higher than those of the parent flavonoid.

Dedicated to Professor Adam Bartecki on the occasion of his 90th birthday.

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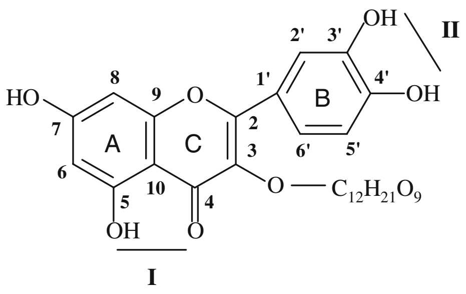


Fig. 1 Possible coordination sites of metal ions in rutin molecule

In [9], it was also shown that the iron and copper complexes of flavonoids were much more effective than the uncomplexed polyphenols in protecting isolated rat hepatocytes against hyposia-reoxygenation injury.

Deng et al. [11] emphasize that flavonoids' (baicalin, hesperidin, naringin, quercetin, and rutin) function as antioxidant mainly depends on chelating iron ions and scavenging peroxyl radicals, whereas their OH radical scavenging effect is much less important. What's more, quercetin and rutin are the most effective in scavenging peroxyl radicals because of their structure—phenolic hydroxyl groups in the B-ring are more liable to peroxyl radical attack.

Experiments on animals [12] (rats) showed that complexation copper(II) ions by rutin increase antioxidant and anti-inflammatory activity of bioflavonoid. Whereas the antioxidant activity of Fe(rut)Cl_3 was much lower and in some cases approached that of rutin.

In [13], it was stated that the selective inhibitory effect of rutin under pathologic conditions induced by iron overload is thought to be due to the formation of inactive iron–rutin complexes which are unable to catalyze the conversion of superoxide ion into reactive hydroxyl radicals, a process responsible for the free radical-mediated toxic effect of iron overload.

In the above-mentioned publications, the examinations were carried out in solutions and they concerned mainly biological properties of rutin complexes with some transition metal ions.

In this article, the synthesis of solid-state complexes of Fe(II) and Fe(III) ions with rutin was carried out. Some of physicochemical properties of the obtained compounds were examined.

Experimental

Apparatus

The elemental analysis for C, H, N, and S was performed with an Elemental Analyser EA 1108 apparatus (Carbo Erba, Italy). The contents of iron were determined by a gravimetric and spectrophotometric methods (spectrophotometer SPECOL 10, Carl Zeiss Jena, Germany). The thermogravimetric analysis was carried out in air using an OD-102 derivatograph, F. Paulik-J. Paulik-L. Erdey system (MOM, Hungary). The UV–Vis spectra of the complexes in water and methanol were taken with a Beckman DU-640 spectrophotometer (Beckman, Germany). IR spectra were made on FTIR spectrophotometer model IFS 66/S (BRUCKER, Ettlingen, Germany). Measurements of magnetic susceptibility of the complexes of Fe(II) and Fe(III) with rutin were made with a Quantum Desigon SQUID magnetometer (type MPMS-5).

Reagents

Solutions (0.1 and 0.05 mol dm^{-3}) of rutin (Koch-Light Laboratories Ltd., UK) were obtained by dissolving the appropriate weighed amounts of compounds in methanol. 0.1 mol dm^{-3} solutions of iron(II) and iron(III) sulfate(VI) were obtained by dissolving the appropriate weighed amounts of the salts in redistilled water and acidifying them with a 1 mol dm^{-3} H_2SO_4 solution. All reagents were analytically pure. The solutions were prepared directly before synthesis.

Preliminary tests

In order to estimate the optimal pH value of iron(II) and iron(III) complexation by rutin, the preliminary tests were carried out in methanol-aqueous solutions (1:1) using spectrophotometric method. The absorbance dependence of wavelength and pH was determined. Two series of solutions were prepared.

Series I—$c_M:c_L = 1:5$, series II—$c_M:c_L = 5:1$ (c_M and c_L—molar concentration of metal and ligand, respectively); the tested solutions were green–yellow. pH within 3–7 was fixed with 0.01 mol dm^{-3} NaOH and H_2SO_4 solutions. The spectra in the range 300–800 nm were taken on SPECORD UV VIS spectrophotometer (Carl Zeiss Jena) at 293 ± 1 K.

In visible region was observed:

- for Fe(II) over pH = 4 bathochromic shift of ligand band by 6 nm and inflexion formation at $\lambda = 417$ nm,
- for Fe(III) over pH = 4.5 inflexion at $\lambda = 417$ nm.

On the basis of examinations, pH = 5.5 was chosen as the optimal environment of iron complexation by rutin.

Synthesis of complexes

The synthesis of the complexes was carried out using an excess of metal ions with relation to the ligand;

c_M:c_L = 5:1 and with the ligand excess in relation to metal cations, c_M:c_L = 1:5. To this end, an appropriate volume of rutin was mixed with an appropriate volume of the initial metal ion solution at room temperature. The syntheses were carried out in methanol-aqueous solutions (1:1), and pH = 5.0 were fixed with 0.10 and 0.01 mol dm^{-3} NaOH solutions. The time of each reaction was 8, 96, and 196 h. Amorphous sediment precipitated, which, after appropriate time, was filtered off and rinsed several times in methanol-aqueous solutions (1:1). Next, the sediments were dried in air at room temperature. All obtained compounds were black, only Fe(III)–rutin complexes, c_M:c_L = 5:1 (96 and 196 h), characterized by metallic lustre.

Composition of complexes

The contents of C, H, and S in the compounds under investigation were determined using a Carbo Erba EA-1108 elemental analyser. The amount of iron was established by the spectrophotometric and gravimetric methods [14]. The gravimetric (drying at 393 K) and derivatographic methods were applied to find the content of crystallization water in the complexes.

Anal. Calcd. for (**1**) $FeOH(C_{27}H_{29}O_{16})\cdot 5H_2O$ ($c_{Fe^{2+}}$:c_L = 1:5; regardless of synthesis time): C, 41.98; H, 5.22; Fe, 7.23; H_2O, 11.66. Found: C, 42.35; H, 5.16; Fe, 7.36; H_2O, 11.50. Anal. Calcd. for (**2**) $Fe_2OH(C_{27}H_{27}O_{16})\cdot 9H_2O$ ($c_{Fe^{2+}}$:c_L = 5:1, regardless of synthesis time): C, 36.10; H, 5.16; Fe, 12.43; H_2O, 18.05. Found: C, 35.80; H, 4.75; Fe, 12.48; H_2O, 18.00. Anal. Calcd. for (**3**) $Fe(OH)_2(C_{27}H_{29}O_{16})\cdot 8H_2O$ ($c_{Fe^{2+}}$:c_L = 1:5, regardless of synthesis time): C, 38.44; H, 5.62; Fe, 6.62; H_2O, 17.09. Found: C, 38.73; H, 5.29; Fe, 6.46; H_2O, 17.00. Anal. Calcd. for (**4**) $[Fe_6(OH)_2(4H_2O)(C_{15}H_7O_{12})SO_4]\cdot 10H_2O$ ($c_{Fe^{2+}}$:c_L = 5:1, 96 and 196 h): C, 16.43; H, 3.40; S, 2.92; Fe, 30.56; H_2O, 16.43. Found: C, 16.13; H, 3.47; S, 2.87; Fe, 30.82; H_2O, 16.10.

At an excess of iron(III) ions with regard to rutin under the synthesis conditions, a side reaction of rutin oxidation occurs—its equilibrium establishes after 96 h. It was stated that in a shorter time of reaction a mixture with indeterminate composition forms.

Thermogravimetric analysis

The investigation was carried out in air under the following conditions: sensitivity TG—100 mg, temperature 293–1273 K, DTA—1/15, DTG—1/5, time 100 min. The results were listed in Table 1 and presented, for selected compound, in Fig. 2.

Spectral measurements

The UV–Vis spectra of rutin and its complexes were taken in water and methanol (Figs. 3 and 4). The infrared spectra were carried out in KBr pellets in the range 4000–400 and 600–50 cm^{-1}, the samples were powered and suspended in the Nujol mull and were then inserted between two polyethylene windows. Table 2 lists the results of the UV–Vis spectral examination and the oscillation frequencies of the chosen infrared bands.

Magnetic measurements

Measurements of magnetic susceptibility of the complexes of Fe(II) and Fe(III) with rutin were made with a Quantum Desigon SQUID magnetometer (type MPMS-5) in the temperature range from 2 to 300 K and magnetic field of 5 kOe. The contribution of the support cell was independently measured and subtracted. The correction for diamagnetism of the constituent atoms was calculated using Pascal's constants [15] and found to be -3.79×10^{-4}, -5.22×10^{-4}, -5.11×10^{-4}, -4.83×10^{-4} cm^3 mol^{-1}

Table 1 Temperature values of thermal decomposition of rutin complexes with Fe(II) and Fe(III)

ΔT_1 (K)	T^{DTG}_{min}	ΔT_2 (K)	T_k (K)	% H_2O		nH_2O	% Residue mass		Final decomposition product
				Calc.	Obtain.		Calc.	Obtain.	
(**1**) $FeOH(C_{27}H_{29}O_{16})\cdot 5H_2O$									
293–463	393	463–1053	1053	11.7	11.5	5	10.3	10.0	Fe_2O_3
(**2**) $Fe_2OH(C_{27}H_{27}O_{16})\cdot 9H_2O$									
293–423	363	423–1063	1063	18.0	18.0	9	17.8	17.5	Fe_2O_3
(**3**) $Fe(OH)_2(C_{27}H_{29}O_{16})\cdot 8H_2O$									
293–453	363	453–1053	1053	17.1	17.0	8	9.5	9.0	Fe_2O_3
(**4**) $[Fe_6(OH)_2(4H_2O)(C_{15}H_7O_{12})SO_4]\cdot 10H_2O$									
293–383	333	443–1273	–	16.4	17.0	10	Continuous loss of mass was observed at 1273 K		
383–443	393								

ΔT_1 (ΔT_2), temperature range corresponding to dehydration endoeffect of definite amount of water molecules (corresponding to decomposition of anhydrous compound); T^{DTG}_{min}, temperature corresponding to minimum on DTG curve; T_k, temperature of final product formation

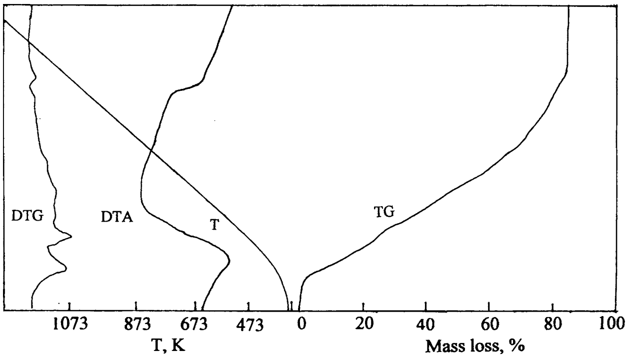


Fig. 2 TG, DTG, and DTA curves of compound (**2**) in air

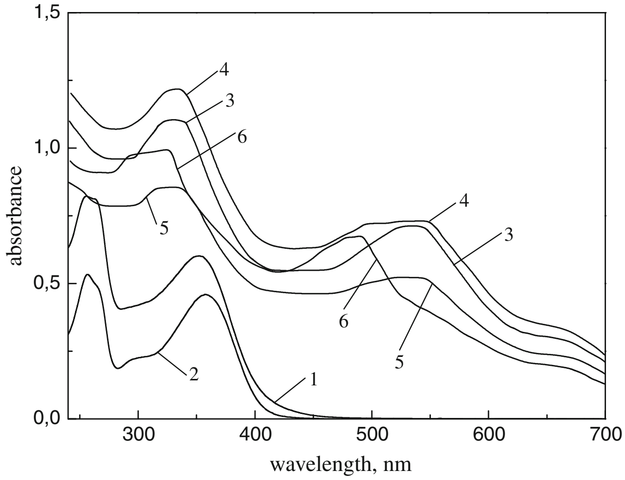


Fig. 3 Absorption spectra in visible and ultraviolet ranges of water and methanol solutions of rutin and rutin–Fe(II) complexes ($l = 1$ cm): *1* rutin in water, *2* rutin in methanol ($c = 3.00 \times 10^{-5}$ mol dm^{-3}), *3* $FeOH(C_{27}H_{29}O_{16})\cdot 5H_2O$, (**1**) (water), *4* $FeOH(C_{27}H_{29}O_{16})\cdot 5H_2O$, (**1**) (methanol), *5* $Fe_2OH(C_{27}H_{27}O_{16})\cdot 9H_2O$, (**2**) (water), *6* $Fe_2OH(C_{27}H_{27}O_{16})\cdot 9H_2O$, (2) (methanol). Saturated solutions unless stress differently

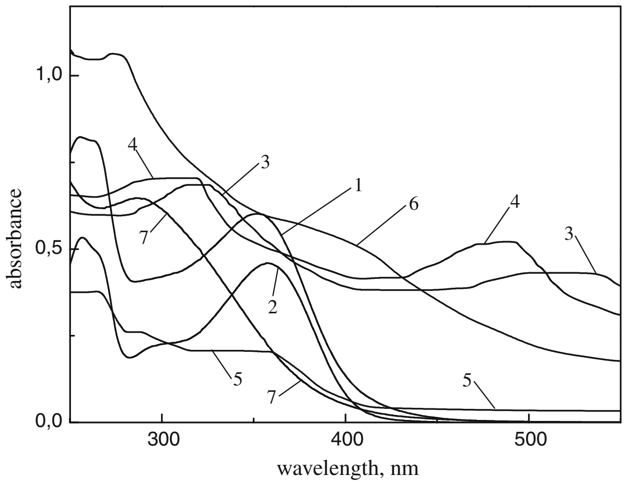


Fig. 4 Absorption spectra in visible and ultraviolet ranges of water and methanol solutions of rutin and rutin–Fe(III) complexes ($l = 1$ cm): *1* rutin in water, *2* rutin in methanol ($c = 3.00 \times 10^{-5}$ mol dm^{-3}), *3* $Fe(OH)_2(C_{27}H_{29}O_{16})\cdot 8H_2O$, (**3**) (water), *4* $Fe(OH)_2(C_{27}H_{29}O_{16})\cdot 8H_2O$, (**3**) (methanol), *5* $[Fe_6(OH)_2(4H_2O)(C_{15}H_7O_{12})SO_4]\cdot 10H_2O$, (**4**) (water), *6* $[Fe_6(OH)_2(4H_2O)(C_{15}H_7O_{12})SO_4]\cdot 10H_2O$, (**4**) (methanol), *7* solution from above complex precipitate $[Fe_6(OH)_2(4H_2O)(C_{15}H_7O_{12})SO_4]\cdot 10H_2O$ after 96 h. Saturated solutions unless stress differently

per molecule of complexes (**1**)–(**4**), respectively. The effective magnetic moments were calculated using the formula: $\mu_{\mathrm{eff}} = 2.83(\chi_M \cdot T)^{1/2}$ B.M., where χ_M magnetic susceptibility of the iron ions with an allowance for diamagnetism, T temperature in K. For the investigated compounds, the Weiss constants (Θ) were calculated from the least squares fitting of the $1/\chi_M$ versus T curves. The Curie constants (C) were determined from $\chi_M \cdot T = f(T)$ dependence for T equals 300 K.

Results and discussion

Synthesis of the complexes of Fe(II) and Fe(III) with rutin

Due to mixing methanol-aqueous solutions of iron cations and rutin at pH = 5.5, black, amorphous deposits precipitate. It was found that the composition of the complexes depends on the synthesis conditions. If there is an excess of ligand in the solution, (**1**) $FeOH(C_{27}H_{29}O_{16})\cdot 5H_2O$ and (**3**) $Fe(OH)_2(C_{27}H_{29}O_{16})\cdot 8H_2O$ complexes appear. However, in the case of metal cation excess, a iron complexes of the (**2**) $Fe_2OH(C_{27}H_{27}O_{16})\cdot 9H_2O$ and (**4**) $[Fe_6(OH)_2(4H_2O)(C_{15}H_7O_{12})SO_4]\cdot 10H_2O$ compositions are formed.

Compounds directly after educe from reaction mixture are well soluble in water, slightly in methanol. After being air dried, they are sparingly soluble in water as well as methanol (solubility of the order of 10^{-6} mol dm^{-3} at 293 K). Better solubility of wet compounds is the cause of appearance of intermolecular hydrogen bonds. In [16], it was stated that intermolecular hydrogen bonds have an influence on solubility of flavone in ethanol.

In [17–19], it was stated that apart from complexation, the oxidation reactions between some metal ions and flavonoids occur. Polihydroxyflavones are oxidizing to quinones in presence of mostly metal cations on the highest oxidation numbers. Ability to reduction is related to redox potential and number of hydroxyl group in flavonoid molecule. Less amount of OH group reduces possibility of hydrogen loss and because of that it reduces ability for flavonoid oxidation and metal reduction. The presence in ring C 2C=3C bound coupling with 4C=O is also very important. The presence of oxidized form of flavonoid could be stated by spectrophotometric method; if in

Table 2 UV–Vis and IR spectra of rutin and the complexes of rutin with Fe(II) and Fe(III)

Compound	UV–Vis							IR band				
	Wavelength (nm)							$\bar{\nu}$ (cm^{-1})				
	Water				Methanol							
	Band I	Band II	Band III	Band IV	Band I	Band II	Band III	4C=O	2C=3C	9C–O–2C	M–O	M–OH
Rutin	–	353	–	258	–	361	258	1653s	1598s	1131w 1120w	–	–
(**1**)	556	413	–	274	556	406	275	1648sh 1618s		1121m	408w	290w
(**2**)	556	406	–	273	556	367	268	1648sh 1618s		1121m	408w	290w
(**3**)	556	397	–	270	556	367	263	1648sh 1618s		1121m	408w	–
(**4**)	–	336	294	256	556	385	274	1618s		1119s	412m-br	290w

Intensity of bands is given by s = strong, m = medium, w = weak; sh, shoulder on strong band; br, broad

UV–Vis range band on $\lambda_{\max}$ in the range 284–294 nm appears [19].

In connection with above mentioned, in this article for all syntheses, UV–Vis spectra for solution from above complex precipitate were performed. It was stated that only in the case of iron(III) complex (c_M:c_L = 5:1) already after 8 h synthesis conduction the oxidation of rutin occurs. Equilibrium of process establishes after 96 h (Fig. 4).

Under the investigation conditions, the aqua-complexes of iron(II), hydroxo-complexes of iron(III), and ligands, rutin ions, sulfate(VI), and hydroxyl ions may occur. The border pH value of hydroxo-complex formation ($\mathrm{pH}_{[\mathrm{MOH}]^+}$) amounts to $\mathrm{pK_w}$—$2 - \log\beta_1$, where β_1 is a first stability constant of appropriate hydroxo-complex [20]. For the investigated metal ions, the $\mathrm{pH}_{[\mathrm{MOH}]^+}$ values are equal:

- $\mathrm{pH}_{[\mathrm{FeOH}]^+} = 7.5(\log\beta_1 = 4.5)$,
- $\mathrm{pH}_{[\mathrm{FeOH}]^{2+}} = 1.0(\log\beta_1 = 11.0)$.

Taking into consideration the above-mentioned data, it seems probable that mixed complexes were formed where flavonoid, sulfate(VI), hydroxyl ions, and water molecule are the ligands. As an example, complexation for (**3**) were described with the following equations:

$$\left[\mathrm{Fe(H_2O)_6}\right]^{3+} + \mathrm{H_2O} \rightleftarrows \left[\mathrm{Fe(H_2O)_5OH}\right]^{2+} + \mathrm{H_3O^+}, \quad (1)$$

$$\left[\mathrm{Fe(H_2O)_5OH}\right]^{2+} + \mathrm{H_2O} \rightleftarrows \left[\mathrm{Fe(H_2O)_4(OH)_2}\right]^{+} + \mathrm{H_3O^+}, \quad (2)$$

$$\left[\mathrm{Fe(H_2O)_4(OH)_2}\right]^{+} + \mathrm{H_3L^-} \rightleftarrows \mathrm{Fe(OH)_2(H_3L)} + 4\mathrm{H_2O}, \quad (3)$$

where $\mathrm{H_3L^-}$—rutin ion existed in solution at pH 5.5 [21].

For aqueous solutions of obtained compounds, the qualitative tests were performed. The presence of iron(II) and iron(III) was checked by means of 2,2′-bipyridine and ammonium thiocyanate, respectively. The analysis reveals that in compounds (**1**) and (**2**) occurs iron(II), compound (**3**) includes iron(III), (**4**) is the mixed valence compound and in this connection could be semiconductor [22]; tentatively carry out conductivity test confirms this presumption.

Thermogravimetric analysis

Thermogravimetric investigation confirmed the elementary analysis results and the composition of the complexes obtained. The acquired temperature data with regard to the composition of the investigated compounds (see Table 1) seem to indicate that the compounds are subject to gradual decomposition with a rise in temperature. The occurrence of endothermal effects (DTA curve) is due to the separation of crystallization water in the temperature range 293–463 K. Further stages of the thermal changes are due to the loss of function groups or the destabilization of the complex structure and burning of organic ligands. The total value of these effects is observed as exothermic effects on the DTA curve. Above 1053 K, the final decomposition product, $\mathrm{Fe_2O_3}$, was formed (see Table 1). The thermolysis of (**4**) complex did not reach equilibrium state in the tested temperature range.

Electronic spectra

UV–Vis spectra of the rutin and the investigated complexes were taken in water and methanol (Figs. 3 and 4). The rutin spectrum in methanol (water) has two $\pi \rightarrow \pi^*$ intensive absorption transfer bands. According to [23, 24], band I, at 361 (353) nm, is considered to be associated with absorption due to the ring B cinnamoyl system (with 3C-sugar group), and band II, at 258 nm, with absorption involving the A ring (with 5C–OH group) benzoyl system.

In the spectra of (**1**) $FeOH(C_{27}H_{29}O_{16})\cdot 5H_2O$, (**2**) $Fe_2OH(C_{27}H_{27}O_{16})\cdot 9H_2O$, and (**3**) $Fe(OH)_2(C_{27}H_{29}O_{16})\cdot 8H_2O$ taken in methanol band I are bathochromically shifted by 45, 6, and 6 nm, respectively, and band II at 258 nm are shifted by 17, 10, and 5 nm, respectively.

The observed changes at bands position might be the evidence for the metal ion being bound by appropriate part of ligand molecule. Coordination of iron in 4C=O and C5–OH position for compound (**1**) causes the largest bands shift. Next, in the case of (**3**), substitution of iron ion in ring B shifts the ligand bands insignificant. The compound (**2**) has two iron ions bounded by 4C=O and C5–OH as well as C3′–OH and C4′–OH [25–27].

However, in (**4**) $[Fe_6(OH)_2(4H_2O)(C_{15}H_7O_{12})SO_4]\cdot 10H_2O$, the lack of sugar group in the position C3–OH makes possible a different way of metal binding which results in different shift values: 24 nm for band II and 16 nm for band I.

Besides, in the spectra of all complexes, there is an intensive at about 556 nm which arises from overlapping charge-transfer band L → M and d–d transitions.

In the spectra of water solutions of (**1**)–(**3**) compounds, the same direction of band shift as in methanol is observed, but their values are much higher; for band II 60, 53, and 44 nm, respectively. These data are a result of different solvation of the central ion in water and methanol [28].

In (**4**), band II is hipsochromically shifted by 17 nm, a position of band IV is practically unchangeable, the new band at 294 nm is observed—this band is connected with oxidized form of rutin. These data strongly suggest that the quinone arising from rutin is the ligand (Scheme 1) and Fe^{2+} and Fe^{3+} are chelated by 5C–OH, 4C=O and 3′C–OH, 4′C–OH systems.

Similar to methanolic solutions, for all obtain complexes a new band at 556 nm was observed.

On the basis of UV–Vis spectra in methanol, the values of splitting in ligands field (Δ) [29] were calculated: (**1**) 21750 cm^{-1}, (**2**) 22100 cm^{-1}, (**3**) 22600 cm^{-1} as well as (4) 26700 cm^{-1}. Obtained Δ pointed that described compounds (**1**)–(**3**) are the complexes of medium field formed by the same ligand (rutin ion); however, (**4**) was formed by oxidized form of rutin (quinone) and is the complex of strong field [30].

Infrared spectra

The IR spectra of the investigated compounds were made within the range 4000–50 cm^{-1}. As diagnostic frequencies, the vibration frequencies of the carbonyl >4C=O and etheric 9C–O–2C– groups, and also Fe–O as well as Fe–OH bounds (see Table 2) were taken into consideration. Complexity of flavonoids IR spectra makes the interpretation difficult. In rutin, spectrum in the same frequencies range bands of sugar moiety and aglycone is observed. Spectra of compounds (**1**)–(**3**) are similar. The different character of (**4**) spectra confirms its different structure.

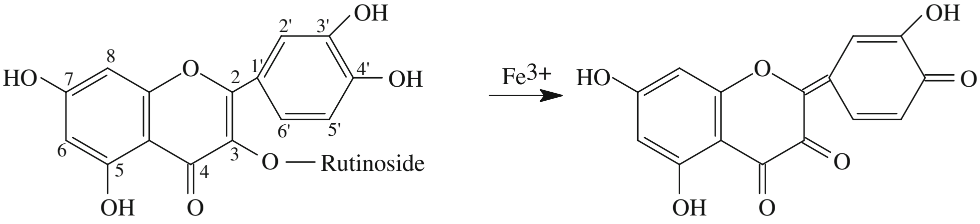
As a result of coordination of iron by rutin, an overlapping band >4C=O (1653 cm^{-1}) with 2C=3C (1598 cm^{-1}) occurs and a strong band at 1618 cm^{-1} is observed. Additionally, in spectra compounds (**1**)–(**3**) a shoulder at 1648 cm^{-1} appears. Symmetrical vibrations band of etheric group in ring C of rutin is split into two frequencies at 1131 and 1120 cm^{-1}. In spectra of complexes, this splitting is not observed but the intensity is changed; this band appears in the range 1121–1119 cm^{-1}. These facts suggest that the oxygen in ring C does not take part in the metal bond; appears a resonance amplifying bound C–O [31].

For compounds (**1**)–(**3**), a new band at 408 cm^{-1} appears, it is related to Fe–O vibration. For (**4**), this band occurs at 412 cm^{-1} shows medium intensity and is significantly broad which may be a result of Fe–O–Fe interaction [32, 33].

The confirmation of formation obtained compounds as hydroxycomplexes is the occurrence of frequencies of Fe–OH group in the far infrared (290 cm^{-1}) [34].

FIR spectra were recorded in order to characterize the participation of sugar group in metal binding and metal–metal bridge formation. The lack of strong, broad band at 200 cm^{-1} is the evidence of lack metal–sugar bound [35].

In the range 260–170 cm^{-1} [34], there is no additional vibration connected with metal–metal interaction.



Scheme 1 Oxidation of rutin by iron(III)

Magnetic measurements

In order to estimate magnetic properties, the oxidation number of metal ions, and the structure of the iron–rutin complexes, the magnetic measurements were carried out. Dependences $\chi_M = f(T)$ and $\mu_{eff} = f(T)$ for all examinated compounds are analogous, shown in Fig. 5.

On the basis of $\chi_M = f(T)$, one may say that for complexes (**1**)–(**4**) as T increased, χ_M smoothly lowered and then tended to a plateau at ca. 100 K. Then the χ_M values are 2.42×10^{-2}, 3.05×10^{-2}, 4.26×10^{-2}, and 7.75×10^{-2} cm^3 K mol^{-1}, respectively. Calculated values of magnetic moments pointed that the obtained complexes are paramagnetic. The values of effective magnetic moments [M.B.] at 300 and 1.9 K are (**1**) 4.82, 3.14, (**2**) 5.45, 3.43, (**3**) 6.18, 3.21, and (**4**) 8.60, 3.18.

For compounds (**1**) and (**2**), magnetic moments at room temperature are very close to values for the free iron ion on +2 (4.90 M.B.) and +3 (5.92 M.B.) oxidation number; however, as temperature decreases, μ_{eff} decreases, reflecting the gradual depopulation of the crystal field (CF) split energy levels of metal ions [36].

On the basis of μ_{eff}, values for complexes (**1**) and (**3**) the spatial structure for them may be predicted. Compounds (**1**) and (**3**) are high-spin complexes with structure similar to tetrahedron and regular octahedron [30, 37].

Complexes (**2**) and (**4**) are polynuclear with intermediate interactions which has an influence to μ_{eff} value.

Compound (**2**) includes two iron atoms on +2 oxidation state which are coordinated in different places in the rutin molecule (positions II and III) and, what follows, the metal–metal interactions did not occur. In this case, the susceptibility of complex is a sum of susceptibilities of individual central ions and a ligand [38].

In hexanuclear complex (**4**), iron atoms at +2 and +3 oxidation state are connected by oxide bridges so the metal–metal interactions may occur which can be observed as decrease in magnetic moment [38].

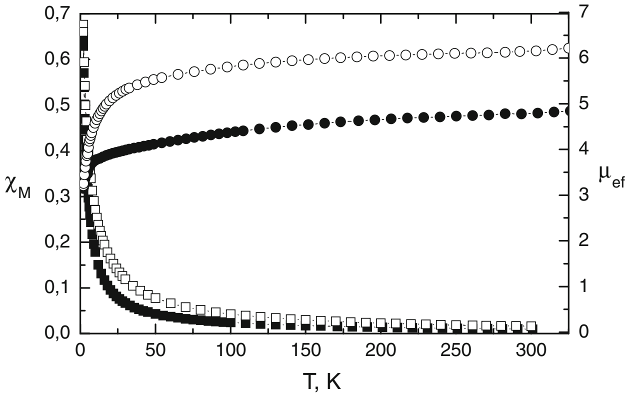


Fig. 5 Experimental magnetic data plotted as magnetic susceptibility χ_M, cm^3 mol^{-1}(■ (**1**); □ (**3**)); and magnetic moment μ_{eff}, B.M. (● (**1**), ○ (**3**)) versus temperature

Complexes (**1**) and (**2**) obey Curie law, and the appropriate Curie constants (C) amount to 2.2 and 2.8 cm^3 K mol^{-1}.

Compounds (**3**) and (**4**) obey the Curie–Weiss law; C and Weiss constants (θ) are equal: for (**3**) C = 4.8 cm^3 K mol^{-1}; $\theta = -8.7$ K; and for (**4**) C = 9.2 cm^3 K mol^{-1}; $\theta = -14.3$ K. This is probably the consequence of antiferromagnetic spin interaction [for compounds (**3**) and (**4**), the Weiss constants have a negative sign] or CF splitting of the paramagnetic spin state—complexes (**1**) and (**2**) [37, 39, 40].

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