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The Titanium(IV), Iron(III) and Manganese(II) Complexes of Chrysin-4′-sulfonate*

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The chrysin-4′-sulfonic acid and its sodium salt (Nachsa-4′) have been synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopy. New complexes of Ti(IV), Mn(II) and Fe(III) ions with chsa-4′ anion in solid state were obtained. Their composition and some physicochemical properties were studied by thermogravimetric analysis, UV/Vis, infrared spectroscopy and magnetic measurements. The structure of the compounds was elucidated on the basis of the results obtained.

Key words: complexes, chrysin-4′-sulfonic acid (Chsa-4′), synthesis, magnetic properties, thermal analysis, spectroscopic properties

Chrysin (5,7-dihydroxyflavon) is one of flavons widely spread in nature as plant dyes. Many of those are biologically active, particularly those able to form quinone group and coordinate metal ions. They are involved in complex redox reactions related to plant photorespiratory system, in solar energy transfer, including the protection against ultraviolet part of radiation. They are important enzyme inhibitors and play a role in protection of lipids, adrenaline and vitamin C. Flavons found many pharmacological applications [1–3].

The quercetin (3,5,7,3′,4′-pentahydroxyflavon), morin (3,5,7,2′,4′-pentahydroxyflavon), and their sulfonate derivatives are the mostly known flavons. Sulfonation of quercetin led to three derivatives: the quercitin-5′-sulfonate, the quercitin-8-sulfonate, and the quercitin-8,5′-disulfonate, which were characterized as sodium salts [4,5]. Sulfonation of morine resulted in formation of the morin-5′-sulfonate [6]. Sulfonate derivatives of flavons are well soluble in water contrary to parent flavons. No sulfonate derivative of chrysin was reported to date. Here, we report the synthesis and spectral characterization of sodium chrysin-4′-sulfonate as well as some of metal ion complexes of chrysin-4′-sulfonate. The chrysin itself is known to form insoluble complexes with metal ions [7–9]. Therefore, we have undertaken the attempts to synthesize analogous complexes with sulfonate derivative to study them in solution.

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*Dedicated to Professors Maria and Stanisław Kopacz on the occasion of their 25-th anniversary of work at Rzeszów University of Technology.

EXPERIMENTAL

Apparatus: Elemental analysis for C, H was performed with an Elemental Analyzer EA 1108 apparatus (Carb Erba). The thermogravimetric analysis was carried out using a Derivatograph OD-102 system F. Paulik-J. Paulik-L. Erdey (MOM, Hungary). The UV/Vis and infrared spectra were taken with Beckman DU 640 and IR PARAGON-1000 (USA) spectrophotometer, respectively. The ^{1}H and ^{13}C NMR spectra of sodium chrysine-4′-sulfonate have been recorded with Bruker Avance 500 MHz instrument in dimethylsulfoxide-d_6 solvent at room temperature. Magnetic measurements were carried out with a Gouy balance.

Syntheses and analytical procedures: Synthesis of the chrysin-4′-sulfonic derivative. 10 g of chrysin was dissolved in 40 ml of concentrated H_2SO_4. The mixture was stirred and heated 48 hours under reflux (423–433 K). After cooling, the reaction mixture was carefully added into 40 ml of distilled water. The precipitated yellow sediment was separated and the crude product was recrystallized several times from water. A jelly-like precipitate was obtained, which was first dried under vacuum. The compound obtained was chrysin-4′-sulfonic acid (Hchsa-4′), which was analyzed as sodium salt (vide infra). The sodium chrysin-4′-sulfonate was obtained by addition of sodium chloride solution into water solution of Hchsa-4′. The yellow precipitate of Nachsa-4′ was separated by concentration of the solution and the crude product was purified by several recrystallizations from water. The crystalline product was isolated as hydrated salt ($C_{15}H_9O_7SNa\cdot 4H_2O$).

Synthesis of the complexes. 100 ml of the stock solution of the salt of the given metal ions was mixed with 100 ml of Nachsa-4′ solution. They were neutralized by ammonia (diluted with water in 1:1 ratio). pH values of precipitation for complexes were: 0.7 for Ti(IV), 5.5 for Mn(II) and 1.5 for Fe(III). The precipitated sediments were separated and washed several times with water and water-methanol (1:1) solution, separated by centrifuging and dried in air at room temperature. The complexes were isolated as water solvates: $Ti(OH)_2(C_{15}H_9O_7S)_2\cdot 8H_2O$, $MnOH(C_{15}H_9O_7S)\cdot 4H_2O$, $FeOH(C_{15}H_9O_7S)_2\cdot 9H_2O$.

Study of the composition. The contents of carbon, hydrogen and sulphur were determined by elementary microanalysis. The contents of appropriate metals were determined by classic complexometric method and basing on thermogravimetric analysis. The crystalline water was determined thermogravimetrically.

Thermographic analysis. Thermogravimetric study was performed in air under the following conditions: TG – 100 mg, DTG – 1/5, DTA – 1/3; 1/10, with 10 deg/min speed. The thermogravimetric results of experiments for all studied compounds are collected in Table 1.

Spectroscopic analysis. The UV/Vis spectra of Ti(IV), Mn(II) and Fe(III) complexes of Chsa-4′ as well as Nachsa-4′ in methanol are presented in Figure 1 and Table 2. The results of infrared spectral examination of all compounds in KBr pellets within 4000–650 cm^{-1} region are listed in Table 3.

The ^{1}H and ^{13}C NMR spectra of Nachsa-4’ have been recorded in DMSO-d_6 solvent at room temperature. The assignment of ^{13}C resonances has been done on the basis of ^{1}H ^{13}C correlation by standard

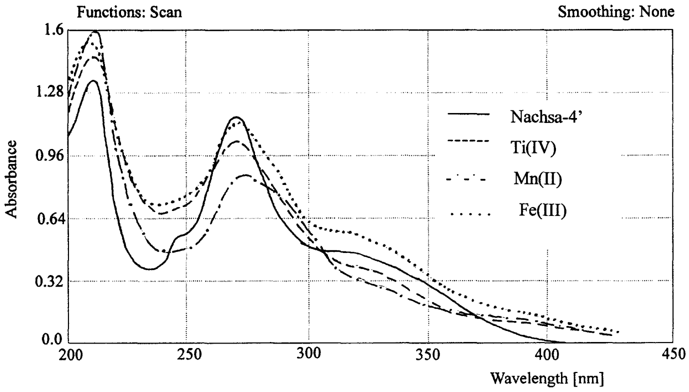

Figure 1. Electronic absorption spectra of Nachsa-4′ and its complexes with Ti(IV), Mn(II) and Fe(III) ions in methanol.

Table 1. Temperature values of thermal decomposition of Nachs and its complexes with Ti(IV), Mn(II) and Fe(III) ions.

Compound	ΔT_1 [K]	$T_{min.}^{DTG}$	ΔT_2 [K]	T_k [K]	nH_2O	% H_2O		% residue mass		Final decomposition product
						Calculated	Obtained	Calcu-lated	Obtained	
$C_{15}H_9O_7SNa{\cdot}4H_2O$	313–398	363	688–1223	1223	3.5	14.72	14.50	16.57	16.5	Na_2SO_4
	398–493	463			0.5	2.10	2.50			
$Ti(OH)_2(C_{15}H_9O_7S)_2{\cdot}8H_2O$	293–543	373	543–1008	1008	10	20.18	20.3	8.94	9.0	TiO_2
$MnOH(C_{15}H_9O_7S){\cdot}4H_2O$	313–593	363	593–1193	1193	5	18.87	18.8	11.51	11.0	Mn
$FeOH(C_{15}H_9O_7S)_2{\cdot}9H_2O$	293–518	353	518–1103	1103	10	19.87	20.5	8.68	8.5	Fe_2O_3

$\Delta T_1(\Delta T_2)$ – temperature range corresponding to dehydration endoeffect of definite amount of water molecules (corresponding to decomposition of anhydrous compound).

$T_{min.}^{DTG}$ – temperature corresponding to minimum on DTG curve.

T_k – temperature of final product formation.

Table 2. Positions of absorption bands and extinction coefficients of Nachsa-4′ and its complexes with Ti(IV), Mn(II) and Fe(III) in methanol ($c_{Nachsa\text{-}4'} = 5.07{\cdot}10^{-5}$ mol/dm^3, $c_{Ti\text{-}chsa\text{-}4'} = 1.75{\cdot}10^{-5}$ mol/dm^3, $c_{Mn\text{-}chsa\text{-}4'} = 3.22{\cdot}10^{-5}$ mol/dm^3, $c_{Fe\text{-}chsa\text{-}4'} = 2.22{\cdot}10^{-5}$ mol/dm^3; l = 1 cm).

Nachsa-4′		$Ti(OH)_2(C_{15}H_9O_7S)_2{\cdot}8H_2O$		$MnOH(C_{15}H_9O_7S){\cdot}4H_2O$		$FeOH(C_{15}H_9O_7S)_2{\cdot}9H_2O$	
ν_0 [a] cm^{-1}	$\varepsilon_{max.}$ [b] mol^{-1} dm^3 cm^{-1}	ν_0 [a] cm^{-1}	$\varepsilon_{max.}$ [b] mol^{-1} dm^3 cm^{-1}	ν_0 [a] cm^{-1}	$\varepsilon_{max.}$ [b] mol^{-1} dm^3 cm^{-1}	ν_0 [a] cm^{-1}	$\varepsilon_{max.}$ [b] mol^{-1} dm^3 cm^{-1}
47169 (212 nm)	38152	47400 (211 nm)	23420	47200 (212 nm)	37490	47400 (211 nm)	77140
40160 (249 nm)	15682	–	–	–	–	–	–
36764 (272 nm)	32682	36900 (271 nm)	59250	36600 (273 nm)	26160	36800 (272 nm)	56920
31645 (316 nm)	13076	30800 (325 nm)	21140	30600 (327 nm)	9660	32500 (308 nm)	28740

[a] Band center.

[b] Mole absorption coefficient at band maximum.

HMQC and HMBC experiments. ^{1}H NMR (chemical shift [ppm], multiplicity, assignment, coupling constant): 6.23 (1H, d, 6-H, $J_{6,8}$ = 2.1 Hz); 6.56 (1H, d, 8-H); 6.94 (1H, s, 3-H); 7.77 (2H, d, 3′,5′-H, $J_{2',3'}$ = 8.3 Hz); 8.04 (2H, d, 2′,6′-H). ^{13}C NMR (chemical shift [ppm], assignment): 94.1 (8-C); 99.0 (6-C); 104.0 (10-C); 105.4 (3-C); 126.0 (3′,5′-C); 126.2 (2′,6′-C); 130.6 (1′-C); 151.3 (4′-C); 157.4 (9-C); 161.4 (5-C); 162.7 (2-C); 164.4 (7-C); 181.8 (4-C).

Magnetic study. Measurements of the magnetic properties of the complexes studied were carried out in the solid state by Gouy's method within 77–302 K. The diamagnetic corrections were applied according to [10]. The values of the effective magnetic moments of the complexes are listed in Table 3.

Table 3. Frequences of characteristic absorption bands in IR spectra (cm^{-1}) and values of effective magnetic moments of chsa-4′ complexes with Ti(IV), Mn(II) and Fe(III) ions.

Hchsa-4′ cm^{-1}	Nachsa-4′ cm^{-1}	Ti(IV)-chsa-4′ cm^{-1}	Mn(II)-chsa-4′ cm^{-1}	Fe(III)-chsa-4′ cm^{-1}	Type of vibrations
3600–2400	3600–2400	3600–2400	3600–2400	3600–2400	ν_{OH} in molecules containing H_2O and –OH groups (hydrogen bonded)
1640	1659	1628	1636	1632	$\nu_{C=O}$ in γ-piron ring
1609	1627	1604	1612	1596	$\nu_{C=C}$ in aromatic ring, δ_{OH} in H_2O molecules, most intensive at about 1600 cm^{-1}
1560	1585	1572	1580	1572	
1505	1519	1560	1552	1560	
1481	1457	1516	1520	1524	
1387	1373	1360	1356	1352	$\delta_{OH\,(ip)}$ most intensive in complexes
1223	1227	–	–	–	
1180	1191	*	*	*	$\nu_{SO2,\,asym.}$; $\nu_{SO2,\,sym.}$
			Magnetic properties		
–			10.63	5.82	θ [K]
			5.78	6.07	$\mu_{eff.}$ [B.M.]

*broad band; θ – Curie-Weiss constant.

RESULTS ADN DISCUSSION

Chrysin undergoes sulfonation at 423–433 K to form monosulfonic derivative. The sodium salt was analyzed as $C_{15}H_9O_7SNa{\cdot}4H_2O$ solvate, based on elemental analysis and thermogravimetric studies (m.p. = 691–692 K). The TG analysis in aerobic condition demonstrated the lost of hydrate water molecules within 313–493 K in an endothermic two-step process. Further increase of temperature up to 688 K resulted in the complex exothermic decomposition of organic anion, leading eventually to the sodium sulfate at 1223 K.

The sodium chrysine-4′-sulfonate revealed a very simple ^{1}H NMR spectrum in dimethylsulfoxide-d_6 solvent. It composes of singlet resonance of 3-H at 6.94 ppm, two weakly coupled resonances from 6-H and 8-H (with J^4 = 2.1 Hz) and AB-type spectrum from aromatic substituent *ortho*- and *meta*-protons, centered at about 8.0

ppm. The comparison of the ^{1}H chemical shifts of Nachsa-4′ with that of chrysin [11] shows a substantial downfield shift of all proton resonances upon sulfonation, *i.e.* Δ(3′,5′-H) = 0.32 ppm; Δ(2′,6′-H) = 0.17 ppm; Δ(3-H) = 0.24 ppm; Δ(6-H) = 0.06 ppm; Δ(8-H) = 0.16 ppm. Similar comparison of ^{13}C NMR spectra gives the largest difference values for carbon substituted with sulfonate (*para*), namely Δ(4′-C) = 19.7 ppm, whereas other phenyl ring resonances remain almost unaltered; Δ(3′,5′-C) = –2.8 ppm; Δ(2′,6′-C) = 0.1 ppm; Δ(1′-C) = –0.1 ppm as well as those of flavon ring system.

There are two absorption bands in the 240–350 nm region of the UV/Vis spectrum of Nachsa-4′; the band centered at 316 nm is due to transition localized within B ring of cinamonyl system, whereas that one, centered at 272 nm is consistent with absorbance of ring A of benzoyl system [12]. The $\pi \rightarrow \pi^*$ bands in Nachsa-4′ have higher extinction coefficients in comparison with those in chrysin.

The most diagnostic stretching vibration in infrared spectra of chrysin and their sulfonate derivatives: Hchsa-4′ and Nachsa-4′ is the $\nu_{(C=O)}$, which is centered at 1655 cm^{-1} in the case of chrysin and shifted to 1640 cm^{-1} and 1659 cm^{-1} for Hchsa-4′ and Nachsa-4′, respectively.

The complexes of Ti(IV), Mn(II), and Fe(III) with chsa-4′ anionic ligand were obtained from the mixtures of metal ion salts and the sodium salt of ligand in acidic solutions to avoid the hydrolysis of metal ions, which otherwise took place in presence of large concentration of sodium salt of weakly coordinating oxygen donor ligands. Thus, the complexes were precipitated from aqueous solutions of pH range 0.7–5.5. These procedures have led to formation of mono- and bis-ligand complexes, in which only two – four oxygen donors from chsa-4′ were involved in coordination, the remaining coordination sites being occupied by hydroxy anions and/or water molecules. Obtained complexes, containing sulfonated chrysin derivatives were insoluble in organic solvents and sparingly soluble in water and alcohols, similarly to those of chrysin [7–9]. The solubility of the complexes was about 1×10^{-5} to 10^{-4} mol/dm^3. Thus, we dealt with compounds, for which the solid state analytical methods had to be used in order to establish the coordination mode of the ligands and the number of water molecules coordinated.

In the thermogravimetric analysis of Nachsa-4′$\cdot$4H_2O the two-step dehydration is observed, related to the endothermic loss of 3.5 water molecule at around 398 K, whereas the total dehydration takes place at about 463 K, indicating that one water molecule per two sodium cations is bound more tight. This can be considered as an expected result, due to the fact that sodium cation can adopt six water molecules in the coordination sphere, which are weakly bound. Surprisingly, one of those remains bound stronger to two metal ions. The remaining coordination sites are occupied by oxygen donors from Chsa-4′ anion. For $Ti(OH)_2$(chsa-4′)$_2\cdot 8H_2O$ four molecules of water are released from the hydrate at 393 K, while the dehydration is completed at about 543 K without separation of late step of dehydration (Table 1). In this case for the smaller Ti(IV) cation (0.68 Å ion radius in comparison with 0.97 Å in the case of Na^+ [14]) the coordination sphere of metal ion is populated with two hydroxy anions and four molecules of water, which are lost at temperatures above 393 K and are probably hydrogen-bonded to the first-sphere ligands. It is noteworthy that the dehydration is continued at higher temperatures and spread up to 543 K, and this phenomenon corresponds to release of the next two water molecules, which are formed presumably from hydroxide anions and Chsa-4′ anion hydrogens, or less probably, are formed *via* dehydration of Chsa-4′ itself. In the case of two transition metal ion complexes similar TG pattern, *i.e.* the Mn(OH)(chsa-4′)$\cdot$4H_2O and Fe(OH)(chsa-4′)$_2\cdot$9H_2O is observed. The TG analysis shows that solvate water molecules are quantitatively released from solids at temperatures around 373 K, whereas remaining four and two water molecules, presumably coordinated to metal ions in Mn(II) and Fe(III) complexes, respectively, are released within a broad range of temperature (Table 1). Albeit the latter effect is not well-separated, the thermal patterns clearly show the number of coordinated H_2O/OH ligands. Further increase of temperature causes exothermic processes of combustion of Chsa-4′ ligand in aerobic conditions, eventually leading to Na_2SO_4, TiO_2, Mn, and Fe_2O_3. The coordination mode of Chsa-4′ anions could be interpreted on the basis of infrared spectral comparison between the complexes, Hchsa-4′ and Nachsa-4′ (Table 3). The position of $\nu_{(C=O)}$ was diagnostic for involvement of C(4)=O chromophore in coordination. The bathochromic shift of this band is equal to 31, 23, and 27 cm^{-1} for Ti(IV), Mn(II), and Fe(III), respectively (in comparison reference anionic Chsa-4′ in sodium salt), which is much larger than the 19 cm^{-1} shift accompanying sulfonate group protonation (Hchsa-4′ *vs* Nachsa-4′). Consequently, the Chsa-4′ anions are bound in different way to the Ti(IV), Mn(II),

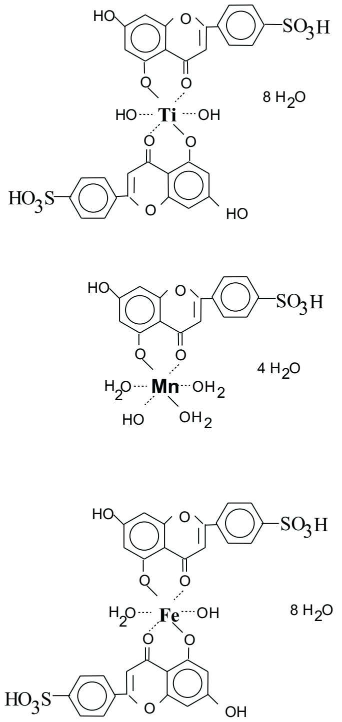

Figure 2. Proposed structures of complexes of Ti(IV), Mn(II) and Fe(III) with Nachsa-4′ in solid state.

and Fe(III) ions than to sodium cation, the most probably *via* C(4)=O and flanking C(5)-oxygen, presumably in anionic form, with sulfonate group remaining protonated. In contrary, the sodium cation in Nachsa-4′ interacts with deprotonated sulfonate anion, although other oxygen donors are involved as well. The spectral picture is completed by UV/Vis spectra of complexes presented in Figure 1. The characteristic feature of the spectra of Ti(IV), Mn(II), and Fe(III) complexes studied is the disappearance of band centered at 249 nm and bathochromic shift of all the bands, well-visible in difference spectra (not presented) and tailing absorbance in visible region of the spectra of Mn(II) and Fe(III) complexes due to weak, spin-forbidden d-d transitions of central metal ions and/or CT M←L bands [13]. The complexes of Chsa-4′ anion with Mn(II) and Fe(III) show a high effective magnetic moment of 5.78 and 6.07 B.M. respectively, which corresponds to five unpaired electrons in the octahedral complexes [10,14]. The studied compounds obey the Curie-Weiss law within the applied temperature range.

Considering the stoichiometry of studied complexes, the number of hydroxy anions and number of first-sphere water molecules, estimated on the basis of TG features, the following formulae of studied complexes have been deduced (Figure 2). The proposed molecular formulae contain the hydroxy anions coordinated to metal ions and protonated sulfonate of Chsa-4′; alternatively the sulfonate can be shown as deprotonated group and consistently the metal ion coordination sites are completed with water molecules.

We are currently working on synthesis of other metal ion complexes and mixed ligand complexes to obtain better soluble species in order to characterize them by crystallographic method. This approach will give us probably more definite characterization of flavon ligands, the multioxygen donors for metal ions.

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