Polish J. Chem., **75**, 1401–1406 (2001)

Physicochemical Properties of the Co(II), Ni(II) and Cu(II) Complexes with Chrysin-4′-sulfonic Acid

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(Received February 1st, 2001; revised manuscript May 17th, 2001)

New solid compounds of Co(II), Ni(II) and Cu(II) with chrysin-4′-sulfonic acid (Hchsa-4′) were obtained. Their composition and some physicochemical properties were studied by thermogravimetric analysis, UV/Vis, infrared and magnetic measurements. Upon heating the hydrated compounds $M(OH)(C_{15}H_9O_7S)\cdot nH_2O$ decomposed to the metal oxides. Structure of the compounds was elucidated on the basis of analytical results.

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

Flavonoids, widely abundant natural products are interesting as pharmacological agents since they stimulate or inhibit a wide variety of enzyme systems and are potential antibacterial, anticancer and antialergic agents [1–3]. Previously [4], the solid complexes of quercetin with Co(II) and Cu(II) of M:L = 2:1 stoichiometry and with Ni(II) of 1:1 stoichiometry as well as the synthesis and physicochemical investigation of the complexes of morin and chrysin with Co(II), Ni(II) and Cu(II) were described. The composition of the complexes obtained at pH = 4–5 was M:L = 1:2 [5,6]. These complexes are sparingly soluble in most solvents, therefore, we have turned towards the sulfonate derivatives of quercetin-5′-sulfonate (Qsa) and morin-5′-sulfonate (Msa) and studied their M:L 1:2 complexes [7,8]. Consequently, we have synthesized another flavonoid sulfonate derivative, *i.e.* chrysin-4′-sulfonic acid (Hchsa-4′) and obtained the complexes of Nachsa-4′ with Ti(IV), Mn(II) and Fe(III) [9].

This paper describes the synthesis of the solid complexes of Co(II), Ni(II) and Cu(II) with chsa-4′ anion. Elemental and thermogravimetric analyses determined the composition. The structure proposed was based on visible and infrared spectroscopies and on magnetic susceptibility measurements.

EXPERIMENTAL

Instruments: Elemental analysis for C, H was performed with an Elemental Analyzer EA 1108 apparatus (Carb Erba). The thermogravimetric analysis was carried out by a Derivatograph OD-102 system F. Paulik-J. Paulik-L. Erdey (MOM, Hungary). The UV-VIS spectra were taken with Beckman DU 640 spectrophotometer. Infrared spectra were recorded with an IR PARAGON-1000 (USA). Magnetic measurements were carried out with a Gouy balance.

Synthesis and analytical analysis: Synthesis of the chrysin-4′-sulfonic acid and analytical procedures were reported previously [9]. For synthetic purposes we have prepared a saturated solution of Hchsa-4′ in water, which was obtained by heating of weighed amount of compound in 100 ml of water. After cooling the remaining undissolved residue was filtered off and solubility of Hchsa-4′ was determined.

Synthesis of the compounds. The complexes of chsa-4′ anion with Co(II), Ni(II) and Cu(II) were obtained as follows: 10 ml of the water solution of the appropriate metal chloride was added into hot saturated aqueous solution of chrysin-4′-sulfonic acid, with continuous stirring, to reach M:L = 1:1 molar ratio. A precipitate was formed, which was washed with copious amount of water-methanol (1:1) solution, separated by centrifuging and dried in air at room temperature. The solubilities of the Co(II), Ni(II) and Cu(II) compounds in methanol at 293 K were determined by UV-Vis spectroscopy.

Analysis of composition. In addition to C, H, S analysis, the content of metals was obtained by two independent methods: Metal ions were determined by classic compleximetric method with EDTA [10], after the samples were dissolved in perchloric acid. In separate experiments the metals were determined by TG analysis, where the metal oxides obtained by heating to 1273 K were determined. Anal. Calcd. for $Co(OH)(C_{15}H_9O_7S)\cdot 4H_2O$: M, 12.24; C, 37.43; S, 6,66; H, 3.77. Found: M, 12.33; C, 37.62; S, 6.92; H, 3.52. Solubility in H_2O: $2.15\cdot 10^{-3}$ mol/dm^3. Anal. Calcd. for $Ni(OH)(C_{15}H_9O_7S)\cdot 4H_2O$: M, 12.20; C, 37.45; S, 6.67; H, 3.77. Found: M, 12.42; C, 37.83; S, 6.85; H, 3.48. Solubility in H_2O: $1.73\cdot 10^{-3}$ mol/dm^3. Anal. Calcd. for $Cu(OH)(C_{15}H_9O_7S)\cdot 2H_2O$: M, 14.13; C, 40.05; S, 7.13; H, 3.14. Found: M, 14.23; C, 39.79; S, 7.38; H, 2.99. Solubility in H_2O: $1.01\cdot 10^{-3}$ mol/dm^3.

Thermographic analysis. Thermogravimetric study was performed in air and the results are collected in Table 1.

Spectroscopic analysis. A study of the electronic absorption spectra in the ultraviolet and visible ranges for the obtained compounds of Co(II), Ni(II) and Cu(II) with Hchsa-4′ in methanol was carried out (Fig. 1). Examination of absorption spectra has been done by standard Gaussian doconvolution. The software PeakFit v.4 for Windows SPSS Inc. was used. Table 2 gives the parameters of the absorption bands of the Hchsa-4' and complexes its anion with Co(II), Ni(II) and Cu(II) in methanol.

The infrared spectra within 4000–650 cm^{-1} were recorded with an IR PARAGON-1000 spectrophotometer on samples prepared in KBr pellets. The wavenumbers of some absorption bands in spectra are listed in Table 3.

Table 1. Temperatures of thermal decomposition of Hchsa-4′ and its complexes with Co(II), Ni(II) and Cu(II) ions.

Compound	T_1 [K]	$T_{min.}^{DTG}$	T_2 [K]	T_k [K]	% Oxide		Final decomposition product
					Calculated	Obtained	
$Co(OH)(C_{15}H_9O_7S)\cdot 4H_2O$	313–553	373	553–1233	1233	15.56	15.2	CoO
$Ni(OH)(C_{15}H_9O_7S)\cdot 4H_2O$	313–538	378	538–1263	1263	15.52	15.0	NiO
$Cu(OH)(C_{15}H_9O_7S)\cdot 2H_2O$	313–553	383	553–1258	1258	17.80	18.0	CuO

$T_1(T_2)$ – temperature range corresponding to dehydration endo effect of definite amount of water particles (corresponding to decomposition of anhydrous compound).
$T_{min.}^{DTG}$ – temperature corresponding to minimum on DTG curve.
T_k – temperature of oxide formation.

Magnetic study. Measurements of the magnetic properties were carried out by Gouy's method within 77-302 K at different magnetic field strength. Effective magnetic moments ($\mu_{eff.}$) were calculated from: $\mu_{eff.} = 2.839\sqrt{\chi_M (T-\theta)}$, where χ_M is molar magnetic susceptibility, T in K, and θ is the Curie-Weiss constant. The molar magnetic susceptibility values (χ_M) for the investigated complexes were calculated from: $\chi_M = M\cdot\chi_g - \chi'$, where M is the molecular mass, χ_g is the gram magnetic susceptibility, and χ' is the sum of the diamagnetic shares of the atoms of the molecule calculated after Pascal [11].

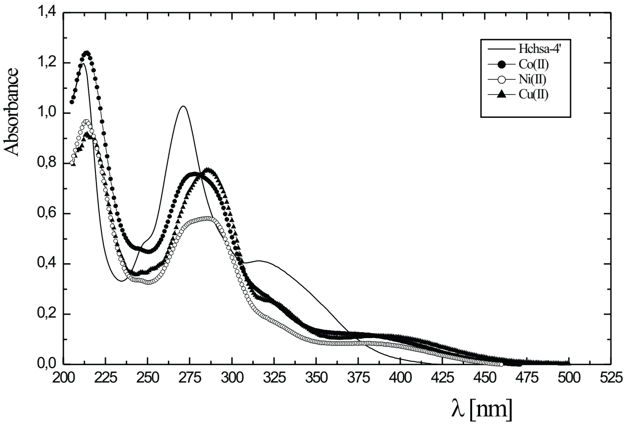


Figure 1. Electronic absorption spectra of Hchsa-4′ and complexes of Co(II), Ni(II) and Cu(II) ions with chsa-4′ anion in methanol.

Table 2. The positions and extinction coefficients of UV/Vis absorption bands of Hchsa-4′ and its complexes with Co(II), Ni(II) and Cu(II) in methanol (Gaussian analysis) ($c_{Hchsa\text{-}4'} = 3.00\cdot10^{-5}$ mol/dm^3, $c_{Co\text{–}chsa} = 3.45\cdot10^{-5}$ mol/dm^3, $c_{Ni\text{–}chsa} = 2.81\cdot10^{-5}$ mol/dm^3, $c_{Cu\text{–}chsa} = 2.89\cdot10^{-5}$ mol/dm^3, l = 1 cm).

Hchsa-4'		Co(OH)($C_{15}H_9O_7S$)·4H_2O		Ni(OH)($C_{15}H_9O_7S$)·4H_2O		Cu(OH)($C_{15}H_9O_7S$)·2H_2O	
ν_0[a] cm^{-1} (nm)	ε_{max}[b] mol^{-1} dm^3 cm^{-1}	ν_0[a] cm^{-1} (nm)	ε_{max}[b] mol^{-1} dm^3 cm^{-1}	ν_0[a] cm^{-1} (nm)	ε_{max}[b] mol^{-1} dm^3 cm^{-1}	ν_0[a] cm^{-1}(nm)	ε_{max}[b] mol^{-1} dm^3 cm^{-1}
47619 (210)	36633	46948 (213)	35739	46948 (213)	34021	46729 (214)	31764
43290 (231)	4300	–	–	–	–	–	–
40816 (245)	10100	40816 (245)	9101	40486 (247)	9502	40322 (248)	7923
37175 (269)	23700	37037 (270)	17072	36900 (271)	12491	36630 (273)	19411
34245 (292)	3167	34245 (292)	14666	34364 (291)	17402	34130 (293)	18373
31250 (320)	10633	30864 (324)	4638	30675 (326)	4306	30960 (323)	6989
–	–	27100 (369)	3652	26455 (378)	3096	25907 (386)	3944
–	–	16260[c] (615)	–	15698[c] (637)	–	14577[c] (686)	–

[a] Position of the band maximum.
[b] Molar absorption coefficient at band maximum.
[c] Position of the band maximum in saturated solution.

Table 3. Position of some bands in IR spectra of Chrysin, Hchsa, Nachsa complexes with metal ions and values of effective magnetic moments of Hchsa-4′ compounds with Co(II), Ni(II) and Cu(II).

Chrysin (cm^{-1})	Hchsa-4′ (cm^{-1})	Nachsa-4′ (cm^{-1})	Co(II)-chsa (cm^{-1})	Ni(II)-chsa (cm^{-1})	Cu(II)-chsa (cm^{-1})	Type of vibrations
1652	1640	1659	1636	1637	1636	$\nu_{C=O}$ in γ-piron ring
–	1223 1179	1227 1191		1250–1150		$\nu_{SO2,\ asym.}$
			Magnetic properties			
–	–	–	–15.1	–7.5	–23.3	θ [K]
–	–	–	5.27	3.32	2.03	$\mu_{eff.}$ [B.M.]
–	–	–	4.7–5.2	2.8–3.3	1.9–2.2	$\mu_{eff.}$ [B.M.]*

* – effective magnetic moments of high-spin complexes of Co(II), Ni(II) in the field of O_h symmetry and T_d symmetry for Cu(II).

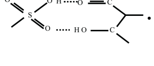
RESULTS AND DISCUSSION

Based on elemental analysis, thermogravimetric studies and complexometric determination of metal ions, the molecular formulas of the compounds obtained are as follows: $Co(OH)(C_{15}H_9O_7S)\cdot4H_2O$ (orange), $Ni(OH)(C_{15}H_9O_7S)\cdot4H_2O$ (light-green) and $Cu(OH)(C_{15}H_9O_7S)\cdot2H_2O$ (green). The complexes are stable in air and can be stored without change of composition. The compounds of Co(II), Ni(II) and Cu(II) are soluble in water. Their solubilities are of the order of 10^{-3} mol dm^{-3} and decrease in the sequence $Co > Ni > Cu$. The physicochemical properties of the compounds obtained were established by thermogravimetric analysis and ultraviolet, visible, infrared spectroscopy and magnetic studies.

All the complexes prepared exhibit similar TG pattern. The measurements were taken in air within 293–1273 K. Decomposition of Co(II), Ni(II) and Cu(II) complexes with Hchsa-4′ exhibits two stages. First stage occurs a total dehydratation. In the second stage the decomposition of the anhydrous compounds takes place, being accompanied by a complex exothermic effect. The final products of the decomposition are the oxides: CoO, NiO, and CuO, which form at 1233, 1263, and 1258 K, respectively.

The study of electronic spectra in ultraviolet and visible range for the complexes of Co(II), Ni(II) and Cu(II) with chsa-4′ anion was carried out in methanol (Fig. 1). The electronic spectrum of Hchsa-4′ in methanol (experimental spectrum) within 200–700 nm has two intensive bands at $\lambda_{max.}=212$ and 269 nm; and a less intensive band at $\lambda_{max.}=315$ nm. It is known that the band at 315 nm is related to the absorbance of the B ring (cinnamonyl system), whereas that at 269 nm is related to the A ring absorbance (benzoyl system). The spectra are consistent with the $\pi\rightarrow\pi^*$ transitions in a ligand molecule [12].

Electronic absorption spectra of the methanol solutions of the complexes exhibit 1–6 nm bathochromic shift of bands of ligand origin (see Table 2), the charge-transfer bands at 369, 378 and 386 nm for Co(II), Ni(II) and Cu(II) complexes respectively, related to the transfer $L\rightarrow M$ [13,14] and bands associated with d-d transitions of the complexes at 615, 637 and 686 nm.

The vibrational spectra of Hchsa-4′ complexes with Co(II), Ni(II) and Cu(II) confirm the structural complexity of the compounds obtained: all show similar solid-state IR spectra. Table 3 presents the frequency bands of $\rangle C{=}O$ and $-SO_3H$ groups. For comparison, the frequencies of the bands for chrysin, Hchsa-4′ and Nachsa-4′ are also listed. From analysis of IR spectra and the frequencies values of the $\rangle C{=}O$ group, one can see, that in Hchsa-4′ spectrum this band shifts towards lower frequencies (1642 cm^{-1}) as compared to this band in chrysin (1653 cm^{-1}), where this value results from the weakening of the carbonyl bond, due to the formation of an intramolecular hydrogen bonded to the hydroxyl group in position 5 (free carbonyl groups have absorptions about 50 cm^{-1} towards higher wave numbers). In an acid molecule this shift probably results in formation of an intermolecular hydrogen bond between $-SO_3H$ and 4CO–5OH group of ligands molecule .

In IR spectrum of sodium salt of Hchsa-4′, this bond is not formed and, therefore, the band frequency of the ⟩C=O group occurs near the frequency for chrysin. On complexation of chsa-4′ anion with Co(II), Ni(II), and Cu(II) a shift of the carbonyl group (C=O) stretching vibration from 1642 cm^{-1} to 1636–1637 cm^{-1} for the complexes may be observed. The shift is consistent with the fact that the group participates in the binding of a metal ion. Sulfonic acids are very easily hydrated, and then should exist as hydronium sulfonates ($R\text{-}SO_3\text{-}H_3O^+$). Therefore, they resemble sulfonate salts with strong absorption in 1230–1120 cm^{-1} (asymmetric SO_2 stretch). All studied compounds are hydrated. The pattern of sulfonic absorption region in IR spectra complexes show a great similarity. The sulfonic group band appearing in Hchsa-4′ at 1223, 1179 cm^{-1} and 1227, 1191 cm^{-1} in sodium salt chrysin sulfonic acid are overlapped in spectra of complexes in this region.

On the basis of spectral data we conclude that in these complexes the chsa-4′ anion is chelated to the central metal ion *via* 4C=O and 5C–O oxygen donors. However, there is one water molecule in complexes (Fig. 2), which does not complete the coordination sphere of the central metal ions. Thus, the straightforward involvement of sulfonate group oxygen donors is rather the dominating interaction between water molecule and sulfonic group of the ligand.

The complex of chsa-4′ anion with Co(II) shows a high effective magnetic moment of 5.27 B.M. at room temperature. It is much higher than the merely spin value equal to 3.83 B.M. for the three non-paired electrons in the octahedral complexes. The difference may result from a considerable share of the orbital component, due to the triple degeneration of the ground state $^4T_{1g}$. In the case of Ni(II) complexes with Hchsa-4′, the effective magnetic moment is 3.32 B.M., which corresponds to two unpaired electrons in octahedral complexes. The high value of the effective magnetic

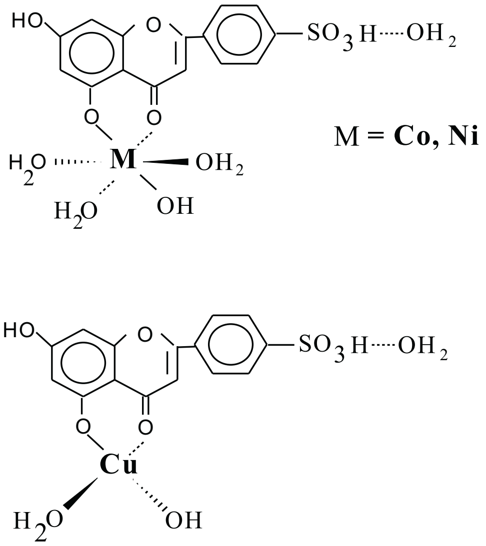


Figure 2. Proposed structure of complexes of Co(II), Ni(II) and Cu(II) with chsa-4′ anion in solid state.

moment of Cu(II) complex of Hchsa-4′ (2.03 B.M. at room temperature) in relation to the pure spin value of 1.83 B.M., evidences the occurrence of an L-S coupling for Cu(II) in the field of T_d symmetry. All the compounds studied obey the Curie-Weiss law within the temperature applied range. All the investigated complexes are high-spin paramagnetic compounds and have a partially distorted octahedral (Co, Ni) or tetrahedral (Cu) structure. Based on these results the following structures of the obtained complex compounds are proposed (Fig. 2).

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