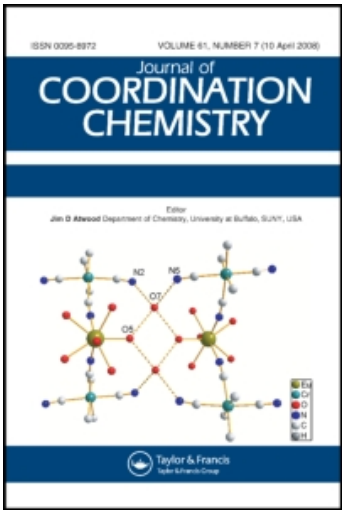

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Characterization and spectroscopic study of new complexes of Cd(II), Hg(II) and Pb(II) with the sodium salt of morin-5'-sulfonic acid

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Characterization and spectroscopic study of new complexes of Cd(II), Hg(II) and Pb(II) with the sodium salt of morin-5′-sulfonic acid

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Solid compounds of Cd(II), Hg(II) and Pb(II) with the sodium salt of morin-5′-sulfonic acid (NaMSA) were obtained. The molecular formula of the complexes are: $Cd(C_{15}H_8O_{10}SNa)_2 \cdot 6H_2O$, $CdOH(C_{15}H_8O_{10}SNa) \cdot 4H_2O$, $Hg(C_{15}H_8O_{10}S) \cdot 4H_2O$ and $Pb(C_{15}H_8O_{10}S) \cdot 3H_2O$. Some of their physicochemical properties such as UV-Vis, infrared, ^{13}C NMR and mass spectra, thermogravimetric analysis, and solubility were studied. On the basis of spectroscopic data NaMSA was bound to Cd^{2+} *via* 4C=O and 3C – oxygen and the Hg^{2+} and Pb^{2+} ions by 5C–OH, 4C=O and 3C–OH.

Keywords: Heavy metals; Sodium salt of morin-5′-sulfonic acid (NaMSA); Complexes; Thermogravimetric; Spectroscopy

1. Introduction

Cadmium, mercury and lead are among the most toxic metals. Intoxication with these metals is mostly related to human activities [1]. Persons poisoned with Cd, Hg and Pb are cured with antidotes forming chelates with metals, e.g. disodium–calcium salt of ethylenediaminetetraacetic acid ($CaNa_2$edta), 2,3-dimercaptopropanol (BAL) antidotum mettallorum (stabilizing solution of hydrogen sulfide) [2]. $CaNa_2$edta is used as an antidote against lead, beryllium and cadmium, whereas BAL counteracts arsenic, mercury, gold, antimony, bismuth, copper, chromium, nickel, cobalt, zinc and lead. The listed chelating reagents are toxic to humans, and new antidotes which might be safely used are sought. Flavonoids and their sulfonic derivatives might be such an antidote. Experiments on animals (rats) showed NaQSA (sodium salt of quercetin-5′-sulfonic acid) to be an antidote against mercury [3, 4], fluorine [5] and chromium(VI) [6] ions.

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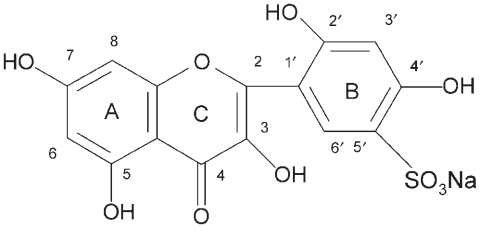


Figure 1. Structure of the sodium salt of morin-5′-sulfonic acid.

NaQSA is soluble in water and totally non-toxic [7]. Also, the sodium salt of morin-5′-sulfonic acid (NaMSA) shows detoxifying properties and its LD_{50} in acute toxicity in Albine Swiss mice and Wistar rats is $1395\,mg\,kg^{-1}$ (result unpublished until now). This toxicity was tested using Litchfiald and Wilcoxon method [8]. Figure 1 shows the structure of NaMSA.

The therapeutic efficacy of NaMSA in acute mercuric chloride poisoning was determined [9]. Wistar rats, divided in control (K) and test groups, were poisoned with a single intragastrical administration of $HgCl_2$ at its LD_{50}. Animals in group K received no treatment, while the test groups (C and D) were treated intragastrically 30 min after poisoning with single doses of NaMSA (50 and $100\,mg\,kg^{-1}$, respectively). Mortality was lower and biochemical indices of renal damage were more satisfactory in group D in comparison with group K. In both tested groups NaMSA diminished mercury absorption and renal mercury accumulation. The authors hint that the mechanism of detoxifying action of NaMSA is based on its ability to form insoluble complexes with mercury ions, which are not absorbed from the digestive tract and are excreted in feces.

Morin is a well-known analytical reagent used for the qualitative and quantitative determination of some metals [10, 11]. A survey of literature data shows that among complexes of flavonoids with Cd, Hg and Pb ions, only lead-morin complexes have been investigated; a crystalline complex of $Pb_3(Morin)_2[CH_3COOH]_2 \cdot 2H_2O$ was characterized [12]. Its absorption maximum in visible range was 420 nm.

Earlier complexes of morin with lead(II) in 40% ethanol-water solutions are described [13]. Absorption maximum for the Pb-Mor complex occurs at 420 nm. The stability constants of PbL^+ and PbL_2 type complexes were determined: $\beta_1 = (2.60 \pm 0.09) \cdot 10^4$ and $\beta_2 = (3.30 \pm 0.26) \cdot 10^9$.

NaMSA [14] complexes with Al, Ga, In [15–17], Co, Ni, Cu [18–21], Fe(II) [22], Fe(III) [23], Ti, Zr, Hf [24] and Cd, Pb [25] ions have been carried out.

NaMSA complexes with Cd(II) and Pb(II) ions in aqueous solutions have been described for the first time [25]. The conditions of ML complex formation at a component molarity ratio ($c_M : c_L$) of 1 : 5 were determined:

– spectrophotometrically, 10^{-5}–$10^{-4}\,mol\,dm^{-3}$, at pH 4.0–5.0
– potentiometric method, 10^{-4}–$10^{-3}\,mol\,dm^{-3}$, at pH 2.5–4.5

In this article the syntheses of solid complexes of Cd(II), Hg(II) and Pb(II) with NaMSA at a different component molarity ratio, $c_M : c_L$, were carried out. The composition, water solubility and structure of the obtained compounds were examined.

2. Experimental

2.1. *Apparatus*

Elemental analysis for C, H, N and S was performed with an Elemental Analyzer EA 1108 apparatus (Carbo Erba, Italy). The contents of appropriate metals were determined by an AAS Perkin Elmer 3100 spectrophotometer (Perkin Elmer, USA). 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 methanol were taken with a Beckman DU-640 spectrophotometer (Beckman, Germany). IR spectra were recorded on an FT-IR Paragon 100 spectrophotometer (Perkin Elmer, USA). The LSI mass spectra were taken with a Finnigan MAT 95 (Finnigan MAT GmbH, Germany). The ^{13}C NMR spectra were recorded with a Bruker Avance DMX 400 MHz instrument.

2.2. *Reagents*

NaMSA was obtained by the method described [26]. Solutions (0.1 mol dm^{-3}) of cadmium(II), mercury(II) and lead(II) nitrate(V) were obtained by dissolving the appropriate weighed amounts of compounds in redistilled water and acidifying them with a 1 : 1 HNO_3 solution. All reagents were analytically pure.

2.3. *Synthesis of complexes*

The synthesis of the complexes was carried out using (1) an excess of metal ions with relation to the ligand and (2) with the ligand excess in relation to metal cations. To this end an appropriate volume of hot (70°C) NaMSA was mixed with an appropriate volume of the initial metal ion solution at room temperature. pH within 1.4–6.0 was fixed with 0.10 and 0.01 mol dm^{-3} NaOH and HNO_3 solutions. After about 30 minutes, flocculent, yellow sediment precipitated which, after three hours, was filtered off and rinsed several times in redistilled water. Next, the sediments were dried in air at room temperature. The conditions of syntheses for the complexes are given below:

System	Conditions		Color	Yield (%)
	$c_M : c_L$	pH		
Cd(II)-NaMSA	1 : 2	6.0	Yellow	30.0
	2 : 1	6.0	Orange-brown	80.0
Hg(II)-NaMSA	1 : 2	1.5	Yellow-orange	38.8
	2 : 1	1.4	Orange (mixture)[a]	–
Pb(II)-NaMSA	1 : 2	2.0	Light yellow	18.0
	2 : 1	2.0	Light yellow	61.0
$c_L = 1{\cdot}10^{-2}$ mol dm^{-3}				

[a]An excess of mercury(II) with regard to ligand under the synthetic conditions gives a side reaction of NaMSA oxidation and a mixture with indeterminate composition.

2.4. *Composition of complexes*

The contents of C, H, N and S in the compounds under investigation were determined using a Carbo Erba EA-1108 elemental analyzer. The amounts of lead, cadmium and sodium were found with a Perkin Elmer 3100 spectrometer, and the mercury content was established by the spectrophotometric method [10]. The gravimetric (drying at 120°C) and derivatographic methods were applied to find the content of crystallization water in the complexes.

Anal. Calcd for $Cd(C_{15}H_8O_{10}SNa)_2 \cdot 6H_2O$, $c_M : c_L = 1:2$ (%): C, 35.08; H, 2.75; S, 6.24; Cd, 10.94; H_2O, 10.52; Na, 4.48. Found: C, 35.10; H, 2.74; S, 5.90; Cd, 11.06; H_2O, 10.00; Na, 4.48. Anal. Calcd for $CdOH(C_{15}H_8O_{10}SNa) \cdot 4H_2O$, $c_M : c_L = 2:1$ (%): C, 29.79; H, 2.83; S, 5.30; Cd, 18.59; H_2O, 11.92; Na, 3.80. Found: C, 29.93; H, 2.76; S, 5.33; Cd, 18.49; H_2O, 11.75; Na, 3.78. Anal. Calcd for $Hg(C_{15}H_8O_{10}S) \cdot 4H_2O$, $c_M : c_L = 1:2$ (%): C, 27.59; H, 2.47; S, 4.91; Hg, 30.72; H_2O, 11.04. Found: C, 28.73; H, 2.33; S, 4.78; Hg, 29.64; H_2O, 10.00. Anal. Calcd for $Pb(C_{15}H_8O_{10}S) \cdot 3H_2O$, $c_M : c_L = 1:2$ and 2:1 (%): C, 28.08; H, 2.20; S, 5.00; Pb, 32.30; H_2O, 8.42. Found: C, 29.26; H, 2.10; S, 5.08; Pb, 32.34; H_2O, 8.38.

No nitrogen was assayed in the compounds.

2.5. *Thermogravimetric analysis*

The investigation was carried out in air under the following conditions: sensitivity TG–100 mg, temperature 20–1000°C, DTA – 1/15, DTG – 1/5, time 100 min. The results are listed in table 1.

2.6. *Spectral measurement*

The UV-Vis spectra of NaMSA and its complexes were taken in methanol (see figure 2).

Infrared spectra were carried out in KBr pellets in 4000–500 cm^{-1}. Table 2 lists the results of the UV-Vis spectral examination and the frequencies of chosen infrared bands.

The ^{13}C NMR spectra of morin, NaMSA and NaMSA complexes with Pb(II) and Cd(II) ions have been recorded in DMSO–d_6 solvent at room temperature. Considering the available literature data [27–34] the assignment of appropriate carbons, indicated on the spectrum, has been made. For the values of the chemical shifts δ, the $\Delta\nu_{1/2}$ bandwidth was determined. ^{13}C NMR (chemical shift [ppm], assignment, bandwidths [Hz] – in the case of complexes);

- Morin: 149.0 (C 2), 136.4 (C 3), 176.4 (C 4), 156.9 (C 5), 93.4 (C 6), 163.7 (C 7), 98.1 (C 8), 161.0 (C 9), 107.0 (C 10), 115.5 (C 1′), 157.1 (C 2′), 103.6 (C 3′), 160.5 (C 4′), 109.5 (C 5′), 131.5 (C 6′);
- NaMSA: 147.9 (C 2), 136.7 (C 3), 176.3 (C 4), 156.3 (C 5), 93.4 (C 6), 163.8 (C 7), 98.1 (C 8), 161.0 (C 9), 103.6 (C 10), 109.4 (C 1′), 157.7 (C 2′), 102.9 (C 3′), 156.9 (C 4′), 122.8 (C 5′), 129.8 (C 6′);
- $Pb(C_{15}H_8O_{10}S) \cdot 3H_2O$: 151.3 (C 2, 25.8), 143.7 (C 3, 96.0), 178.5 (C 4, 25.8), 156.7 (C 5, 12.9), 93.3 (C 6, 64.0), 164.1 (C 7, 12.9), 98.7 (C 8, 64.0), 159.9 (C 9, 25.8), 105.2 (C 10, 64.0), 112.0 (C 1′, 64.0), 159.7 (C 2′, 25.8), 104.5 (C 3′, 64.0), 157.1 (C 4′, 25.8), 123.8 (C 5′, 64.0), 127.2 (C 6′, 64.0);

Table 1. Thermal decomposition of NaMSA complexes with Cd(II) and Pb(II).

				% H_2O			% residue mass		
Δt_1,°C	t_{min}^{DTG}	Δt_2,°C	t_k,°C	Calcd	Obtain.	nH_2O	Calcd	Obtain.	Final decomposition product
$Cd(C_{15}H_8O_{10}SNa)_2 \cdot 6H_2O$									
20–110	80			7.0	6.5	4			$CdCO_3$, Na_2CO_3
		170–650	650				27.1	27.5	
110–170	150			3.5	3.0	2			
$CdOH(C_{15}H_8O_{10}SNa) \cdot 4H_2O$									
20–145	100	145–750	750	11.9	12.0	4	33.0	33.5	CdO, Na_2SO_4
$Pb(C_{15}H_8O_{10}S) \cdot 3H_2O$									
20–170	110	170–650	650	8.4	8.0	3	41.1	43.0	$PbSO_4 \cdot PbO$

Δt_1 (Δt_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.

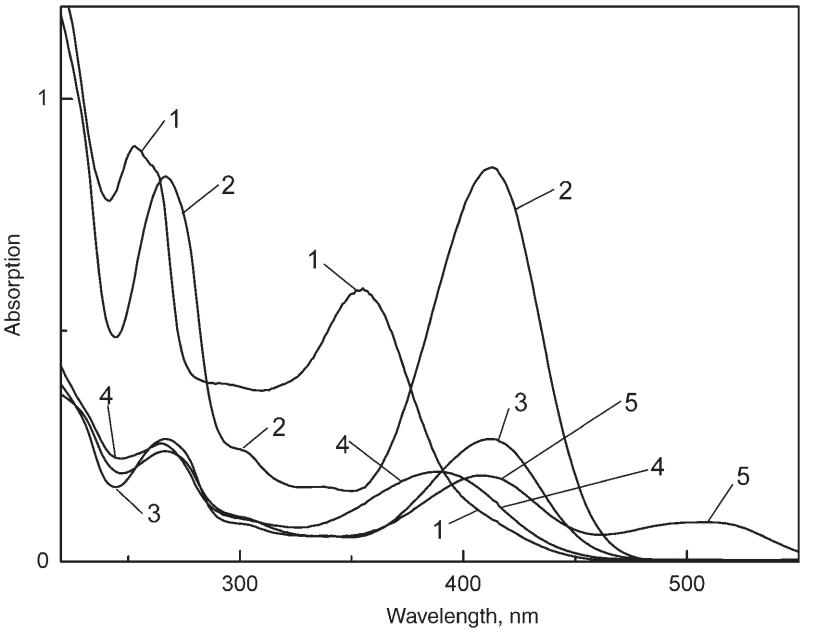
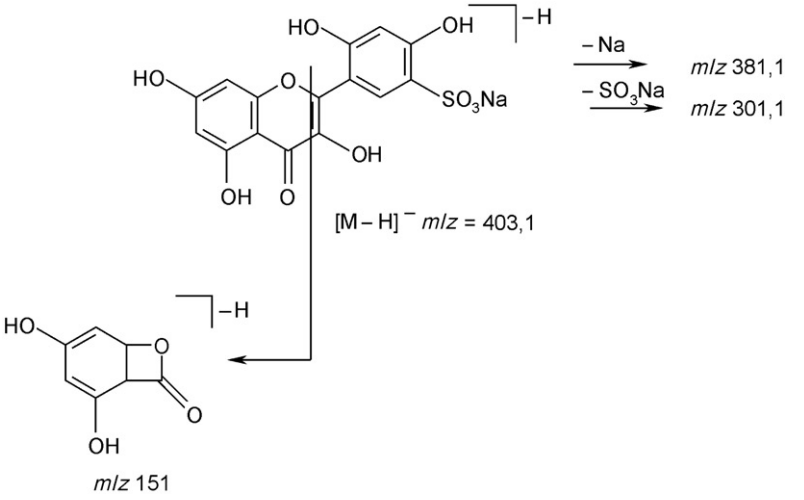


Figure 2. Absorption spectra in visible and ultraviolet ranges of methanol solutions (l = 1 cm): (1) NaMSA ($c = 4.54 \cdot 10^{-5}$ mol dm^{-3}), (2) $Cd(C_{15}H_8O_{10}SNa)_2 \cdot 6H_2O$ ($c = 1.05 \cdot 10^{-5}$ mol dm^{-3}), (3) $CdOH(C_{15}H_8O_{10}SNa) \cdot 4H_2O$ (saturated solution), (4) $Hg(C_{15}H_8O_{10}S) \cdot 4H_2O$ (saturated solution), (5) $Pb(C_{15}H_8O_{10}S) \cdot 3H_2O$ (saturated solution).

- $Cd(C_{15}H_8O_{10}SNa)_2 \cdot 6H_2O$: 148.3 (C 2, 64.0), 140.0 (C 3, 64.0), 176.5 (C 4, 18.2), 156.8 (C 5, 7.3), 93.6 (C 6, 64.0), 164.1 (C 7, 36.4), 98.6 (C 8, 64.0), 160.5 (C 9, 18.2), 105.3 (C 10, 64.0), 112.6 (C 1′, 64.0), 160.0 (C 2′, 18.2), 102.8 (C 3′, 64.0), 157.0 (C 4′, 25.4), 123.7 (C 5′, 64.0), 127.1 (C 6′, 64.0);

Table 2. UV-Vis and IR spectra of NaMSA and the complexes of NaMSA with Cd(II), Hg(II) and Pb(II).

	UV-Vis			IR	
	Wavelength, nm (ε, $m^2 mol^{-1}$)				
Compound	Band I	Band II	Band III	$\nu_{C=O}$	ν_{SO2} as.
NaMSA	Inflexion at 410 nm	357 (1340)	254 (2000)	1661	1192, 1168
$Cd(C_{15}H_8O_{10}SNa)_2 \cdot 6H_2O$	–	415 (4050)	268 (3950)	1653	1176, 1148
$CdOH(C_{15}H_8O_{10}SNa) \cdot 4H_2O$	–	415	268	1650	1176, 1160
$Hg(C_{15}H_8O_{10}S) \cdot 4H_2O$	–	400	265	1640	1167
$Pb(C_{15}H_8O_{10}S) \cdot 3H_2O$	490	410	268	1650	1164



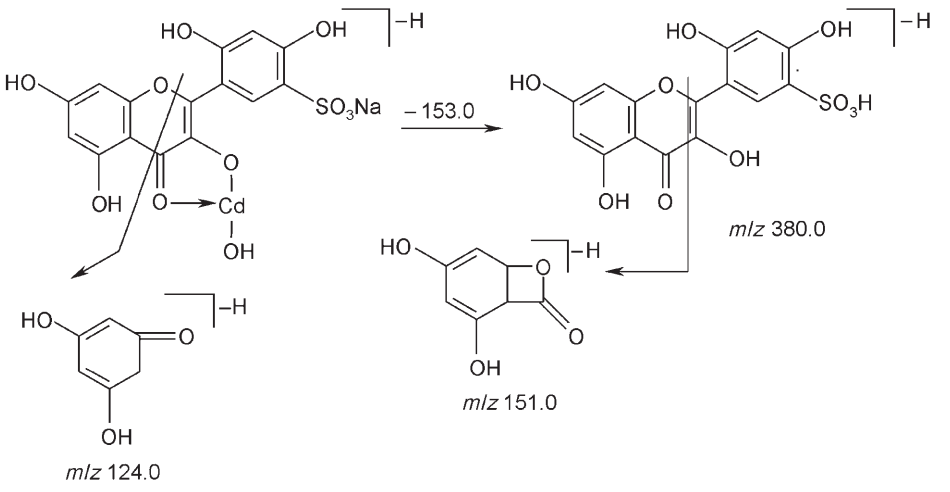
Scheme 1. Fragmentation scheme of $[M–H]^-$ of NaMSA.

- $CdOH(C_{15}H_8O_{10}SNa) \cdot 4H_2O$: 148.3 (C 2, 62.5), 139.8 (C 3, 31.2), 176.4 (C 4, 12.5), 156.8 (C 5, 62.5), 93.6 (C 6, 62.5), 164.1 (C 7, 156.2), 98.6 (C 8, 93.8), 160.4 (C 9, 12.5), 105.2 (C 10, 62.5), 112.4 (C 1′, 62.5), 159.9 (C 2′, 12.5), 102.6 (C 3′, 93.8), 157.0 (C 4′, 12.5), 123.7 (C 5′, 62.5), 127.0 (C 6′, 31.2).

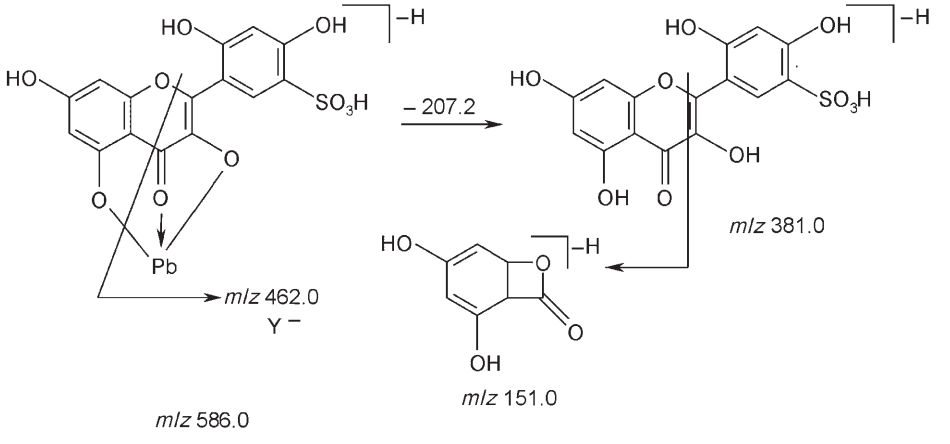
For NaMSA and the $Cd(C_{15}H_8O_{10}SNa)_2 \cdot 6H_2O$, $CdOH(C_{15}H_8O_{10}SNa) \cdot 4H_2O$, $Hg(C_{15}H_8O_{10}S) \cdot 4H_2O$, and $Pb(C_{15}H_8O_{10}S) \cdot 3H_2O$ complexes mass spectra were recorded using the LSI (Liquid Secondary-Ion) technique with 3-nitrobenzyl alcohol as a matrix and acetonitrile as a solvent. The ion source temperature was ~40°C, and accelerating voltage was 4.8 kV. The results are presented in schemes 1–5.

2.7. *Solubility determination*

Solubility determination was carried out in water at 20 and 36°C ± 1°. A particular weight amount of the substances under investigation was thermostated in a precisely measured volume of redistilled water continuously stirred for 12 h. After that, the mixture was filtered on a glass sinter funnel and the residue determined by the weight method.



Scheme 2. Fragmentation scheme of $[M–H]^-$ of $CdOH(C_{15}H_8O_{10}SNa)\cdot 4H_2O$.



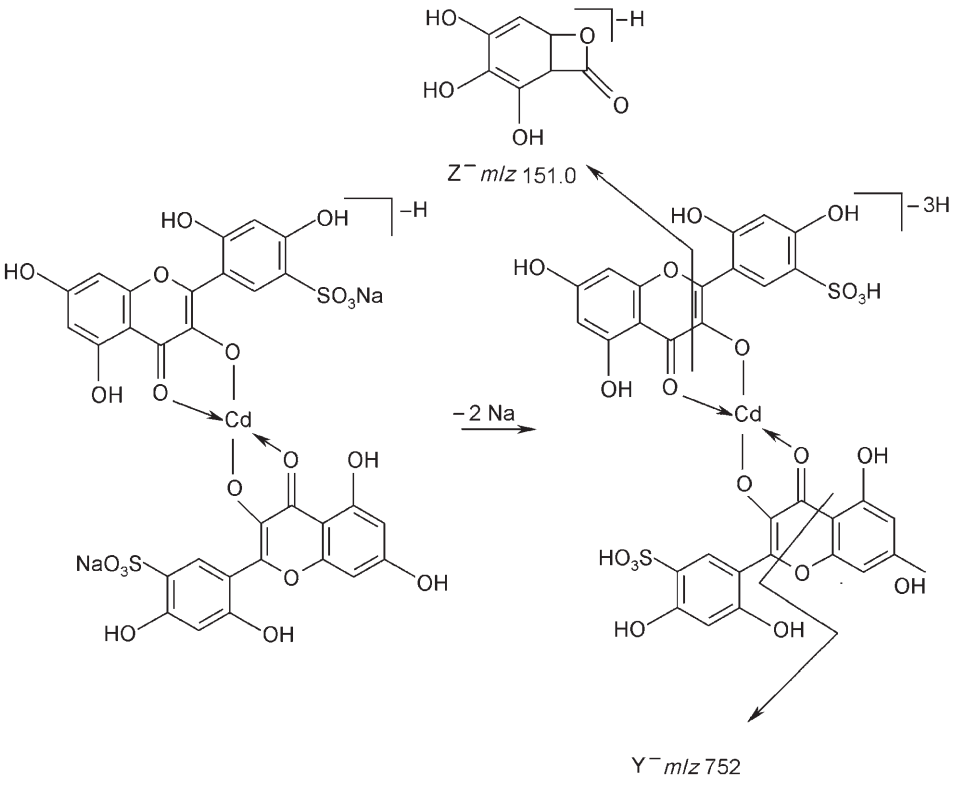
Scheme 3. Fragmentation scheme of $[M–H]^-$ of $Pb(C_{15}H_8O_{10}S)\cdot 3H_2O$.

The filtrate was evaporated at 50°C and the rest was weighed. The subsequent measurements made it possible to define the solubility values in mol dm^{-3} at 20°C (36°C):

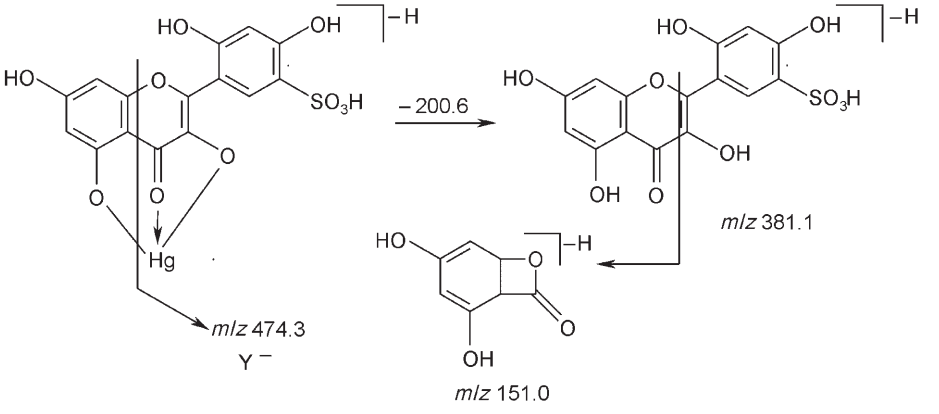
– $Cd(C_{15}H_8O_{10}SNa)_2\cdot 6H_2O$ – $6.91\cdot 10^{-4}$ ($1.04\cdot 10^{-3}$)
– $CdOH(C_{15}H_8O_{10}SNa)\cdot 4H_2O$ – $5.45\cdot 10^{-4}$ ($7.08\cdot 10^{-4}$)
– $Hg(C_{15}H_8O_{10}S)\cdot 4H_2O$ – $9.66\cdot 10^{-4}$ ($1.34\cdot 10^{-3}$)
– $Pb(C_{15}H_8O_{10}S)\cdot 3H_2O$ – $3.94\cdot 10^{-5}$ ($4.92\cdot 10^{-5}$)

3. Results and discussion

The sodium salt of morin-5′-sulfonic acid (NaMSA) is a low-toxic substance ($LD_{50} = 1395$ mg kg^{-1}), well soluble in water [14, 26], and forms stable chelates with different metals, e.g. with toxic metals Cd, Hg, Pb.



Scheme 4. Fragmentation scheme of $[M–H]^-$ of $Cd(C_{15}H_8O_{10}SNa)\cdot 2\cdot 6H_2O$.



Scheme 5. Fragmentation scheme of $[M–H]^-$ of $H_g(C_{15}H_8O_{10}S)\cdot 4H_2O$.

Intragastrically NaMSA administration at a single dose $100\,mg\,kg^{-1}$ lowered the mortality of rats poisoned acutely with $HgCl_2$. Moreover biochemical indices of renal damage were more satisfactory in a group treated with the dose of NaMSA in comparison with a group which received no treatment [9].

3.1. *Synthesis of the complexes of Cd(II), Hg(II) and Pb(II) with NaMSA*

Mixing aqueous solutions of metal cations and NaMSA in an acidic medium gave yellow, flocculent precipitates. In the case of Cd^{2+} and Hg^{2+}, the composition of the complexes depends on the excess of either metal cations or ligand during precipitation. If there is an excess of ligand in the solution, $Cd(C_{15}H_8O_{10}SNa)_2 \cdot 6H_2O$ and $Hg(C_{15}H_8O_{10}S) \cdot 4H_2O$ form. However, in the case of metal cation excess, a cadmium complex $CdOH(C_{15}H_8O_{10}SNa) \cdot 4H_2O$ and a heterogeneous mixture for mercury are formed. The composition of the mercury mixture has not been examined.

On the other hand, Pb^{2+} ions form a complex with NaMSA ($Pb(C_{15}H_8O_{10}S) \cdot 3H_2O$), which shows the same composition regardless of the conditions in which the synthesis is carried out.

Under the investigation conditions only the aquo-complexes of mercury, lead and cadmium occur; the border pH value of hydroxo-complex formation ($pH_{[MOH]^+}$) is $pK_w - 2\log\beta_1$, where β_1 is a first stability constant of appropriate hydroxo-complex [35]. For the investigated metal ions the $pH_{[MOH]^+}$ values are equal:

- $pH_{[CdOH]^+} = 7.7\,(\log\beta_1 = 4.3)$
- $pH_{[PbOH]^+} = 4.5\,(\log\beta_1 = 7.5)$
- $pH_{[HgOH]^+} = 1.7\,(\log\beta_1 = 10.3)$

In the case of $CdOH(C_{15}H_8O_{10}SNa) \cdot 4H_2O$ metal cation excess during precipitation caused mixed complex formation. Such phenomenon did not appear under the synthesis of Pb^{2+} complex. It seems probable that it is because of a larger difference between $pH_{[PbOH]^+}$ and pH of synthesis ($\Delta pH = 2.5$).

Taking into consideration species distribution of NaMSA as a function of pH [26] complexation reactions in aqueous solution can be described with the following equations:

$$\left[Cd(H_2O)_4\right]^{2+} + 2H_4L^{2-}_{(aq)} \rightleftharpoons \left[Cd(H_3L)_2\right]^{4-}_{(aq)} + 2H_2O + 2H_3O^+$$

$$\left[CdOH(H_2O)_3\right]^{+} + H_4L^{2-}_{(aq)} \rightleftharpoons [CdOH(H_3L)]^{2-}_{(aq)} + 2H_2O + H_3O^+$$

$$\left[Hg(H_2O)_4\right]^{2+} + H_5L^{-}_{(aq)} \rightleftharpoons [Hg(H_4L)]_{(aq)} + 3H_2O + H_3O^+$$

$$\left[Pb(H_2O)_n\right]^{2+} + H_5L^{-}_{(aq)} \rightleftharpoons [Pb(H_4L)]_{(aq)} + nH_2O + H_3O^+$$

Because of precipitation at pH 1.4–2.0, the mercury(II) and lead(II) complexes deposit as the acidic form (with $-SO_3H$ group) and the cadmium complexes precipitate at pH 6 as the sodium salt (with $-SO_3Na$ group). After being air dried, the solid complexes are hydrated, with lattice type water joined to –OH and $-SO_3H$ or $-SO_3Na$ ligand groups with a hydrogen bond. The obtained complexes are sparingly soluble in water at 20°C (solubility was about 10^{-5}–10^{-4} mol dm^{-3}) and better soluble at 36°C (about 10^{-3} mol dm^{-3} for cadmium and mercury complexes). The temperature 36°C was chosen as it is near the physiological temperature of the human body.

3.2. *Thermogravimetric analysis*

Thermogravimetric investigation confirmed the elemental analysis results and the composition of the complexes. The acquired temperature data with regard to the composition of the investigated compounds (see table 1) 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 20–170°C. The further stages of thermal change are due to loss of functional groups or destabilization of the complex structure. The changes are accompanied by exothermic events (DTA curve). Above 650°C, the final decomposition products, oxides and salts of the appropriate metal were formed (see table 1). The thermolysis of the Hg-MSA complex is rapid, which makes interpretation impossible.

3.3. *Electronic spectra*

UV-Vis spectra of the investigated complexes were taken in methanol. The NaMSA spectrum in methanol has two $\pi \rightarrow \pi^*$ intense bands (357 and 254 nm). Band I, at 357 nm, is associated with absorption due to the ring B cinnamoyl system (with 3C–OH group) and band II, at 254 nm, with absorption involving the A ring (with 5C–OH group) benzoyl system [36, 37].

In the Cd, Hg and Pb complexes with NaMSA, bands I and II are bathochromically shifted by 43–57 nm and 11–14 nm, respectively.

The observed large changes at band I position might be evidence for the metal binding this part of the ligand.

In the spectrum of the Pb-MSA complex, there is an intensive charge-transfer band at about 430 nm (see figure 2), suggesting that a metal cation–ligand bond may be different from those in other complexes.

Zirconium(IV) and antimony(III) were used for structural investigation of flavonoids [38]. It was stated that for Zr^{4+} excess in relation to flavonoids, in acidic medium, metal interacts with the 3-hydroxy-4-keto and 5-hydroxy-4-keto systems simultaneously and the large bathochromic shift of band I (80 nm for Zr-quercetin) is observed. These data strongly suggest that Pb^{2+} is simultaneously chelated by both 3C–OH, 4C=O and 5C–OH, 4C=O systems and the two chelate rings (five- and six-membered) are formed.

NaMSA binds with Cd^{2+} and Hg^{2+} through 3C–OH and 4C=O or 5C–OH and 4C=O.

3.4. *Infrared spectra*

The IR spectra of the investigated compounds were recorded between 4000–500 cm^{-1}. Assignment of the frequencies is consistent with the literature [27, 39–41]. The coordination of NaMSA could be interpreted on the basis of vibration frequencies of the 4C=O and SO_2 groups in the morin, morin-5′-sulfonic acid (MSA), NaMSA, and complexes of Cd, Hg and Pb with NaMSA (see table 2). In MSA, a shift of the carbonyl band to lower frequencies (1644 cm^{-1}) in relation to the position of that band in morin (1664 cm^{-1}) is probably due to the intramolecular hydrogen bond, formed with the strongly acidic hydrogen of the sulfonic group [42]. In NaMSA, sodium bound in the sulfonic group does not directly interact with the 4C=O group, hence the frequency of

the carbonyl group in NaMSA is 1661 cm^{-1} approaching the value observed in morin (1664 cm^{-1}). In complexes of NaMSA with Cd(II), Hg(II) and Pb(II), the band of the 4C=O group with lower intensity occurs at frequencies of 1640–1653 cm^{-1}, shifted, on average by 8–21 cm^{-1}, to lower values in comparison with NaMSA. This is evidence of metal binding with the carbonyl group [43].

For NaMSA, two frequencies, 1192 and 1168 cm^{-1}, are assigned to the sulfonic group, whereas the MSA spectrum shows only one band at 1174 cm^{-1}. In the spectra of the complexes of Hg(II) and Pb(II) only one SO_2 absorption can be observed (at 1167 and 1164 cm^{-1}, respectively), indicating that these complexes are in the acidic form ($–SO_3H$). The sulfonic group frequencies in Cd-NaMSA spectra are similar to those in NaMSA, evidence of precipitation of the complex as the sodium salt ($–SO_3Na$). Elemental analysis also confirms the presence of sodium in Cd-NaMSA complexes and its lack in other compounds.

Similarity of the $Cd(C_{15}H_8O_{10}SNa)_2 \cdot 6H_2O$ and $CdOH(C_{15}H_8O_{10}SNa) \cdot 4H_2O$ spectra suggests a similar structure. The most probable is formation of the five-membered stable chelate ring 4C=O $\cdots$ Cd–O–3C–, indicated by the shift of the 4C=O band in the Cd complexes towards higher frequencies (1650–1653 cm^{-1}) in relation to the 4C=O band in MSA [27, 44]. If the metal cation occupies a position at 5C–OH and 4C=O groups and six-membered chelates are formed as in the complexes of the sulfonic derivative of chryzin (5,7-dihydroxyflavone) [45, 46], then the carbonyl band is shifted to lower frequencies in relation to MSA. In $Hg(C_{15}H_8O_{10}S) \cdot 4H_2O$, the vibration frequency of the 4C=O band occurs at 1640 cm^{-1}, lower than the MSA band (1644 cm^{-1}). These facts suggest that the 4C=O, 3C–OH and 5C–OH groups take part in the metal bond.

On the basis of the carbonyl frequency shift in $Pb(C_{15}H_8O_{10}S) \cdot 3H_2O$ in relation to MSA by $\Delta\nu = 11\ cm^{-1}$ (see table 2), binding by the carbonyl group is affirmed.

3.5. *NMR spectra*

The ^{13}C NMR spectra of morin, NaMSA and the Cd, Hg, Pb-NaMSA complexes have been recorded in DMSO-d_6 solvent at room temperature.

In the NaMSA spectrum, the number of resonances does not exceed the number of carbons, indicating that there is only one molecule in the asymmetric unit of the crystal [28]. Furthermore, a strong effect of substituent on the C 5′ chemical shift of 13.3 ppm in relation to morin and some changes on neighboring C 6′ and C 4′ were observed. We note that an increase of shielding of 6.1 ppm for NaMSA can be observed for C 1′. It is likely that this difference reflects a change in the angle of phenyl ring torsion caused by substitution of the $–SO_3Na$ group.

In the Pb-MSA spectrum, the shifts of C 3 ($\Delta\delta = -7.0$ ppm), C 4 ($\Delta\delta = -2.2$ ppm) and C 10 ($\Delta\delta = -1.6$ ppm) are connected with a decrease of the electronic deficiency on the appropriate carbons. This is accompanied with a significant increase of half-width for C 3 ($\Delta\nu_{1/2} = 96.0$ Hz) and confirms the site of Pb ion coordination through 5C–OH, 4C=O and 3C–OH groups. The most important difference of the Cd-NaMSA spectra are observed for C 3, which is shifted downfield by 3.3 ppm in $Cd(C_{15}H_8O_{10}SNa)_2 \cdot 6H_2O$ and 3.1 ppm for $CdOH(C_{15}H_8O_{10}SNa) \cdot 4H_2O$. For both Cd-NaMSA complexes, the changes of C 10 by 1.7 and 1.6 ppm, respectively, and a lack

of C 4 shift are observed, suggesting that a metal cation-ligand bond may be different (3C–OH and 4C=O) from those in the Pb^{2+} complex.

Sodium substitution in sulfonic derivative of flavonoid does not cause the shift of resonances in the ^{13}C NMR spectrum [34]. Thus, the differences between Cd and Pb spectra come from different coordination and not complex precipitation in acidic ($–SO_3H$, Pb complex) or salt form ($–SO_3Na$, Cd-NaMSA).

Metal ion substitution creates various intramolecular interactions, e.g. the change of the rotation and rocking of the lateral phenyl ring that leads to changes in the 1′, 2′, 3′, 5′ and 6′ carbon signals. Similar changes are described [27] for Ln-morin complexes.

3.6. *Measurement of mass spectra*

The LSI mass spectra confirm the composition and determine the structure of the investigated complexes. The literature widely describes the application of mass spectrometry to identify flavonoids in plant extracts [47–50]. Moreover, [50] the elucidation of flavonoid isomers was accomplished by ESI-MS/MS *via* formation and collisional activated dissociation (CAD) of Co, Cu, Ni – flavonoid complexes containing an auxiliary ligand (piridyl). Using this technique, the fragments of metal-flavonoid complex can be observed. Earlier [51], ESI MS measurements were performed to study the iron and copper chelation by flavonoids.

The application of fast atom bombardment mass spectrometry (FAB MS) in organometallic, coordination and related compounds study was presented [52].

Negative ion LSI mass spectra of NaMSA showed the $[M–H]^-$ ion as the base peak (m/z 403.1). Also the $[M–H–Na]^-$ and $[M–H–SO_3Na]^-$ ions were detected in the product ion mass spectra. The fragmentation scheme of NaMSA is given in scheme 1.

The spectra of complexes collected in the negative ion mode show the $[M–H]^-$ molecular ions.

In the spectra of the complexes studied in this article, except for $Cd(C_{15}H_8O_{10}SNa)_2 \cdot 6H_2O$, a peak related to the free ligand (MSA) appeared. The fragmentation of $[M–H]^-$ of $CdOH(C_{15}H_8O_{10}SNa) \cdot 4H_2O$ is shown in scheme 2. For deprotonated $Cd(C_{15}H_8O_{10}SNa)_2 \cdot 6H_2O$, $Hg(C_{15}H_8O_{10}S) \cdot 4H_2O$, and $Pb(C_{15}H_8O_{10}S) \cdot 3H_2O$ complexes fragmentation of the dehydrated molecules were observed, as illustrated in schemes 3–5. Cross-ring cleavage of the C-ring in the ligand led to the Y^- product ion m/z 752.0, 474.3 and 462.0, respectively.

In each case the Y^- ion contains the suitable metal ion and the fragment of ligand molecule with 3C–OH and 4C=O groups, evidence for the metal ion being bound by this group.

4. Conclusions

The reactions of Cd(II), Hg(II) and Pb(II) ions with NaMSA in aqueous solutions at pH 1.4–2.0 (Hg, Pb) and 6.0 (Cd) lead to precipitation of chelate complexes. The composition and structure of the complexes depends on the conditions of the

synthesis and the metal ion: Pb^{2+} ions form $Pb(C_{15}H_8O_{10}S)\cdot 3H_2O$; Cd^{2+} and Hg^{2+} ions precipitate as $Cd(C_{15}H_8O_{10}SNa)_2\cdot 6H_2O$ and $Hg(C_{15}H_8O_{10}S)\cdot 4H_2O$ at an excess of ligand; an excess of metal ions leads to formation of $CdOH(C_{15}H_8O_{10}SNa)\cdot 4H_2O$ and a heterogeneous mixture for mercury. On the basis of UV-Vis, IR, LSI MS and ^{13}C NMR analyses the site of metal ion addition to NaMSA is proposed: in cadmium complexes the metal is chelated by 3C–OH and 4C=O and for mercury and lead compounds by 5C–OH, 4C=O and 3C–OH. Formation of sparingly-soluble compounds of NaMSA with Cd(II), Hg(II) and Pb(II) ions and the literature data concerning the therapeutic efficacy of NaMSA in acute mercuric chloride poisoning suggests that NaMSA could be an antidote against the above mentioned metals.

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