

## Complexes of Cadmium(II), Mercury(II) and Lead(II) with Quercetin-5'-sulfonic Acid (QSA)

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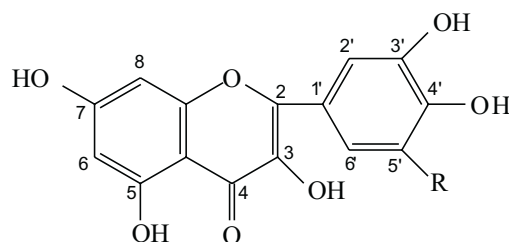
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QSA ( $C_{15}H_{10}O_{10}S \cdot 5H_2O$ ), a ligand, which is non-toxic and well soluble in water, forms complex compounds with cations of toxic metals (Cd, Hg, Pb). New complex compounds with QSA:  $Cd(C_{15}H_9O_{10}S)_2 \cdot 10H_2O$ ,  $Hg(C_{15}H_9O_{10}S)_2 \cdot 8H_2O$ ,  $Pb(C_{15}H_9O_{10}S)_2 \cdot 8H_2O$  and  $Pb(C_{15}H_8O_{10}S) \cdot 4H_2O$  have been synthesized. Some of their physicochemical properties such as UV-VIS and infrared spectra, mass spectra, thermogravimetric analysis, and solubility were studied. It was found that the obtained compounds are sparingly soluble in water, which points out that QSA could be an antidote against cadmium, lead and mercury. The structures of the obtained compounds have been proposed.

**Key words:** complexes, quercetin-5'-sulfonic acid (QSA), synthesis, thermal analysis, spectroscopic properties, antidotes against metals

Cadmium, mercury and lead belong to the most toxic metals. Cases of intoxication with these metals are mostly related to human activities. There are three major ways of the metals being absorbed by the human organism: the alimentary canal, the skin and the respiratory system. These metals exhibit manifold activities that are harmful to health, which, in extreme cases, result in death. Persons poisoned with these metals are cured with antidotes such as the substances forming chelates with metals, e.g. disodium-calcium salt of ethylenediaminetetraacetic acid ( $CaNa_2edta$ ), 2,3-dimercaptopropanol (BAL), antidotum metallorum. The  $CaNa_2edta$  compound is used as an antidote against lead, beryllium and cadmium. The BAL compound is a counterpoison against arsenic, mercury, gold, antimony, bismuth, copper, chromium, nickel, cobalt, zinc and lead [1]. The listed chelating reagents are toxic for the human body, therefore, new antidotes are being sought, which might be safely used. Such an antidote might be quercetin-5'-sulfonic acid (QSA) or its sodium salt (NaQSA). QSA is a derivative of quercetin, well soluble in water and totally non-toxic. Fig. 1 shows the structure of quercetin, QSA and NaQSA. QSA forms sparingly soluble chelate compounds with heavy metal ions. Experiments on animals (rats) showed NaQSA as an active antidote against mercury ions.

Earlier [2,3], complexes of Cd(II) and Pb(II) ions with QSA in aqueous solutions were studied and their stability constants were determined. A complex of Pb(II) with QSA, in the solid state, at a component molarity ratio ( $c_{Pb(II)}:c_{QSA}$ ) of 1:1 was also synthesized.



**Figure 1.** Structures of quercetin ( $R = H$ ), quercetin-5'-sulfonic acid (QSA,  $R = SO_3H$ ) and sodium salt of quercetin-5'-sulfonic acid (NaQSA,  $R = SO_3Na$ ).

In [4] crystalline complexes of quercetin (Q) and morin (Mor) with Pb(II) ions are described. Formation of  $Pb_3Q_2 \cdot 2H_2O$  and  $Pb_3(Mor)_2[CH_3COOH]_2 \cdot 2H_2O$  complexes was observed and their absorption maxima in visible range were 450 and 420 nm, respectively.

In [5] complexes of quercetin and morin with lead(II) ions in 40% ethanol-water solution are described. Absorption maxima occur at 420 nm for the Pb–Mor complex and at 425 nm for the Pb–Q compound. The stability constants of  $PbL^+$  and  $PbL_2$  type complexes (where L – appropriate ligand) were determined:  $\beta_1 = (2.30 \pm 0.14) \cdot 10^5$  and  $\beta_2 = (2.17 \pm 0.34) \cdot 10^{10}$  for lead(II) and quercetin complex, and  $\beta_1 = (2.60 \pm 0.09) \cdot 10^4$  and  $\beta_2 = (3.30 \pm 0.26) \cdot 10^9$  for the complex of lead(II) with morin.

Taking into consideration prospective application of QSA as counterpoison against cadmium, mercury and lead, a synthesis of solid state complexes of Cd(II), Hg(II) and Pb(II) ions with QSA was carried out under the following conditions: with an excess of QSA in relation to metal cations and an excess of metal cations in relation to the ligand, in a acid medium close to pH of gastric juice. Their composition, water solubility and structure were examined.

## EXPERIMENTAL

**Apparatus:** Elemental analysis for C, H and S was performed with an Elemental Analyser EA 1108 apparatus (Carbo Erba). The thermogravimetric analysis was carried out using an OD-102 derivatograph, F. Paulik-J. Paulik-L. Erdey system (MOM Hungary). The UV-VIS and infrared spectra were taken with Beckman DU-640 and FT-IR Paragon 100 (Perkin Elmer, USA) spectrophotometers, respectively. The LSI and Electrospray mass spectra were taken with Finnigan MAT 95 (Finnigan MAT GmbH, Germany) and a Waters/Micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard Apparatus syringe pump, respectively.

**Reagents:** QSA was obtained by the method described in [6]. Solutions ( $0.1 \text{ mole/dm}^3$ ) of cadmium(II) nitrate(V), mercury(II) nitrate(V) and lead(II) nitrate(V) were obtained by dissolving the appropriate weighed amounts of the compounds in redistilled water and acidified with a 1:1  $HNO_3$  solution. All the reagents were analytically pure.

**Synthesis of complexes:** 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. In the first case,  $100 \text{ cm}^3$  of a hot, 0.001 M QSA solution was added to the same amount of an 0.005 M solution of the appropriate metal ions at pH 1.4–1.7. In the second case,  $100 \text{ cm}^3$  of a hot 0.005 M QSA solution was completed with the same amount of 0.001 M of the appropriate metal ions solution at pH = 1.3–1.5. After about 30 minutes, a flocculent sediment precipitated which, after three hours, was fil-

tered off and rinsed several times in redistilled water. The colours of dried sediments were changed from yellow to dark-brown, for Pb, Hg and Cd complexes, respectively.

**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 amounts of lead and cadmium were found with Perkin Elmer 3100 spectrometer, and the mercury content was established by the spectrophotometric method [7]. The gravimetric (drying at 120°C) and derivatographic methods were applied to find the content of crystallization water in the complexes. Analyses confirmed the compositions: **Cd(C<sub>15</sub>H<sub>9</sub>O<sub>10</sub>S)<sub>2</sub>·10H<sub>2</sub>O** (disregarding synthesis conditions), **Hg(C<sub>15</sub>H<sub>9</sub>O<sub>10</sub>S)<sub>2</sub>·8H<sub>2</sub>O** (*c<sub>M</sub>:c<sub>L</sub>* = 1:5, where *c<sub>M</sub>*, *c<sub>L</sub>* – mole concentrations of metal and ligand, respectively), **Pb(C<sub>15</sub>H<sub>9</sub>O<sub>10</sub>S)<sub>2</sub>·8H<sub>2</sub>O** (*c<sub>M</sub>:c<sub>L</sub>* = 1:5), **Pb(C<sub>15</sub>H<sub>8</sub>O<sub>10</sub>S)·4H<sub>2</sub>O** (*c<sub>M</sub>:c<sub>L</sub>* = 5:1). At an excess of mercury(II) ions with regard to ligand, there occurs a side reaction of QSA oxidation and a polymer complex forms whose composition is being examined.

**Thermogravimetric analysis:** The investigation was carried out in air under following conditions: sensitivity TG – 200 mg (QSA, Pb–QSA and Hg–QSA complexes), TG – 100 mg (Cd–QSA), temperature 20–1000°C, DTA – 1/15, DTG – 1/5, time 100 min. The results are listed in Table 1.

**Table 1.** Thermogravimetric analysis results of QSA and its complexes with Cd(II), Hg(II) and Pb(II) ions.

Temperature effects [°C]		Mass loss TG curve, %		Decomposition products within given temperature range [°C]
DTA	DTG	Calculated	Obtained	
<b>C<sub>15</sub>H<sub>10</sub>O<sub>10</sub>S·5H<sub>2</sub>O</b>				
120(–)	105	19.1	19.0	40–160°C; 5H <sub>2</sub> O (crystall. water)
345(–)	340	28.4	28.0	160–400°C; 5H <sub>2</sub> O, CO <sub>2</sub>
490(+)		52.5	53.0	400–980°C; SO <sub>3</sub> , 14C + 14O <sub>2</sub> = 14CO <sub>2</sub>
<b>Cd(C<sub>15</sub>H<sub>9</sub>O<sub>10</sub>S)<sub>2</sub>·10H<sub>2</sub>O</b>				
100(–)	80	12.0	12.0	20–130°C; 7H <sub>2</sub> O (crystall. water)
180(–)	175	5.1	5.0	130–200°C; 3H <sub>2</sub> O (crystall. water)
	290	6.8	7.0	200–310°C; 4H <sub>2</sub> O (constitutional water)
	330	8.5	9.0	310–345°C; 5H <sub>2</sub> O (constitutional water)
480(+)	420	51.6	51.0	345–590°C; 3/2SO <sub>3</sub> , 2CO <sub>2</sub> , 28C + 28O <sub>2</sub> = 28CO <sub>2</sub>
		15.9	16.0	590–1000°C; 1/2(CdO + CdSO <sub>4</sub> )
<b>Hg(C<sub>15</sub>H<sub>9</sub>O<sub>10</sub>S)<sub>2</sub>·8H<sub>2</sub>O</b>				
95(–)	80	13.0	13.5	20–120°C; 8H <sub>2</sub> O (crystall. water)
220(–)	210	18.1	18.0	120–230°C; Hg
280(–)	270	21.9	19.0	230–315°C; 9H <sub>2</sub> O (constitutional water), SO <sub>3</sub>
490(+)		48.4	49.5	315–1000°C; SO <sub>3</sub> , 3CO <sub>2</sub> , 27C + 27O <sub>2</sub> = 27CO <sub>2</sub>
<b>Pb(C<sub>15</sub>H<sub>9</sub>O<sub>10</sub>S)<sub>2</sub>·8H<sub>2</sub>O</b>				
75(–)	80	3.2	3.0	20–95°C; 2H <sub>2</sub> O (crystall. water)
150(–)	145	9.7	9.0	95–175°C; 6H <sub>2</sub> O (crystall. water)
280(–)	290	8.1	8.0	175–310°C; 5H <sub>2</sub> O (constitutional water)
300(–)				

Table 1 (continuation)

440(+)	55.3	56.0	310–855°C; 4H <sub>2</sub> O (constitutional water), 3/2SO <sub>3</sub> , 2CO <sub>2</sub> , 28C + 28O <sub>2</sub> = 28CO <sub>2</sub>
	23.6	24.0	855–1000°C; 1/2(PbSO <sub>4</sub> ·PbO)
			Pb(C <sub>15</sub> H <sub>9</sub> O <sub>10</sub> S) <sub>2</sub> ·4H <sub>2</sub> O
115(–)	125	10.9	10.0 20–165°C; 4H <sub>2</sub> O (crystall. water)
	365	38.3	38.0 165–560°C; 4H <sub>2</sub> O, (constitutional water), 1/2SO <sub>2</sub> , 5/2CO <sub>2</sub> , 13/2C + 13/2O <sub>2</sub> = 13/2CO <sub>2</sub>
510(+)	10.9	11.5	560–860°C; 6C
	39.9	40.5	860–1000°C; 1/2(PbSO <sub>4</sub> ·PbO)

(–) endothermic effect, (+) exothermic effect.

**Measurement of mass spectra:** The electrospray ionization (ESI) mass spectra were recorded for QSA and its complexes with cadmium, lead and mercury metal ions. The sample solutions were prepared in methanol at a concentration of about 10<sup>–5</sup> M. The solutions were infused into the ESI source using a Harvard pump at a flow rate of 20 μl min<sup>–1</sup>. The ESI source potentials were capillary 3 kV, lens 0.5 kV, extractor 4 V and cone voltage 30. Source temperature was 120°C and desolvation temperature was 300°C. Nitrogen was used as the nebulizing and desolvation gas at flow-rates of 100 and 300 l h<sup>–1</sup> respectively. For QSA and the Cd(C<sub>15</sub>H<sub>9</sub>O<sub>10</sub>S)<sub>2</sub>·10H<sub>2</sub>O and Pb(C<sub>15</sub>H<sub>9</sub>O<sub>10</sub>S)<sub>2</sub>·8H<sub>2</sub>O complexes mass spectra were recorded using the LSI (Liquid Secondary-Ion) technique. Glycerin was used 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 listed in Table 2.

**Table 2.** ESI and LSI mass spectra of quercetin (Q), QSA and the complexes of QSA with Cd(II), Hg(II) and Pb(II) ions.

Compound	ESI		LSI	
	m/z	Assignments	m/z	Assignments
Quercetin (Q)	301.0	Q	301.1	Q
			192.9	F 2
			150.9	F 3
			109.0	F 1
QSA	763.0	2QSA	381.1	QSA
	381.0	QSA	300.1	Q
			151.0	F 3
			109.0	F 1
Cd(C <sub>15</sub> H <sub>9</sub> O <sub>10</sub> S) <sub>2</sub> ·10H <sub>2</sub> O	873.0	Cd(QSA) <sub>2</sub>	751.4	CdQSA + F 4
	763.0	2QSA	381.3	QSA
	381.0	QSA	151.2	F 3
Pb(C <sub>15</sub> H <sub>9</sub> O <sub>10</sub> S) <sub>2</sub> ·8H <sub>2</sub> O	763.0	2QSA	968.7	Pb(QSA) <sub>2</sub>
	381.0	QSA	763.2	2QSA
			578.3	PbQSA

Table 2 (continuation)

			381.4	QSA
			300.5	Q
			151.2	F 3
Pb(C <sub>15</sub> H <sub>8</sub> O <sub>10</sub> S)·4H <sub>2</sub> O	763.0	2QSA	–	–
Hg(C <sub>15</sub> H <sub>9</sub> O <sub>10</sub> S) <sub>2</sub> ·8H <sub>2</sub> O	762.0	2QSA	–	–
	641.0	2(Hg(QSA) <sub>2</sub> )		
	381.0	QSA		

**Spectral measurement:** The spectra of UV-VIS, QSA and its complexes were taken in methanol. The infrared spectra were carried out in KBr pellets in 4000–500 cm<sup>-1</sup>. Table 3 lists the oscillation frequencies of the chosen infrared bands.

Table 3. Frequencies of chosen infrared bands of quercetin (Q), QSA, NaQSA and the complexes of QSA with Cd(II), Hg(II) and Pb(II) ions.

IR, cm <sup>-1</sup>	Compound						
	Q	QSA	NaQSA	Cd(QSA) <sub>2</sub> ·10H <sub>2</sub> O	Hg(QSA) <sub>2</sub> ·8H <sub>2</sub> O	Pb(QSA) <sub>2</sub> ·8H <sub>2</sub> O	Pb(QSA)·4H <sub>2</sub> O
$\nu_{C=O}$	1673	1640	1665	1656	1652	1654	1653
$\nu_{SO_2}$	–	1178	1184	1182	1181	1181	1178
$\nu_{M-O}$	–	–	472, 510	547, 525, 464	525, 468	525, 510, 466	522, 507, 462

**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 hours. After that the mixture was filtered on a G-5 glass sinter funnel and the residue determined by the weight method. The filtrate was evaporated at 50°C and the rest was weighed. The subsequent measurements made it possible to define the solubility values listed in Table 4.

Table 4. Water solubility of the complexes of Cd(II), Hg(II) and Pb(II) with QSA.

Compound	Solubility in 20°C ± 1°C		Solubility in 36°C ± 1°C	
	g/100 cm <sup>3</sup> H <sub>2</sub> O	c, M	g/100 cm <sup>3</sup> H <sub>2</sub> O	c, M
Cd(C <sub>15</sub> H <sub>9</sub> O <sub>10</sub> S) <sub>2</sub> ·10H <sub>2</sub> O	5.56·10 <sup>-2</sup>	5.27·10 <sup>-4</sup>	1.30·10 <sup>-1</sup>	1.23·10 <sup>-3</sup>
Pb(C <sub>15</sub> H <sub>9</sub> O <sub>10</sub> S) <sub>2</sub> ·8H <sub>2</sub> O	4.81·10 <sup>-2</sup>	4.32·10 <sup>-4</sup>	5.06·10 <sup>-2</sup>	4.54·10 <sup>-4</sup>
Pb(C <sub>15</sub> H <sub>8</sub> O <sub>10</sub> S)·4H <sub>2</sub> O	2.08·10 <sup>-2</sup>	3.16·10 <sup>-4</sup>	2.71·10 <sup>-2</sup>	4.10·10 <sup>-4</sup>
Hg(C <sub>15</sub> H <sub>9</sub> O <sub>10</sub> S) <sub>2</sub> ·8H <sub>2</sub> O	3.97·10 <sup>-2</sup>	3.58·10 <sup>-4</sup>	5.61·10 <sup>-2</sup>	5.07·10 <sup>-4</sup>

## RESULTS AND DISCUSSION

Quercetin-5'-sulfonic acid (QSA) is a substance, which is totally non-toxic and well soluble in water. It forms complexes with metals toxic for the human body. As new reagents are continually sought to be used as antidotes against heavy metals, the authors of this paper have investigated the synthesis of the complexes of some chosen toxic metals like Cd, Pb and Hg with QSA. During the initial experiments with rats it was found that QSA could be an active counterpoison against mercury. Binding the toxic cation by QSA produces a sparingly soluble chelate and leads to its subsequent removal from the organism.

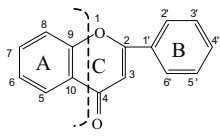
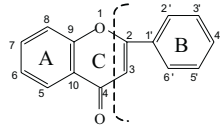
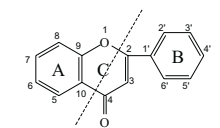
**Synthesis of the complexes of Cd(II), Hg(II) and Pb(II) with QSA:** The synthesis of the complexes is relatively simple; due to mixing aqueous solutions of metal cations and QSA (at pH 1.3–1.7) yellow, flocculent deposit precipitates. It was found that in the case of  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  ions 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,  $\text{ML}_2 \cdot 8\text{H}_2\text{O}$  ( $\text{M} = \text{Pb}$  or  $\text{Hg}$ ) complexes appear. However, in the case of metal cation excess, there forms a lead complex of the  $\text{Pb}(\text{C}_{15}\text{H}_8\text{O}_{10}\text{S}) \cdot 4\text{H}_2\text{O}$  composition and a polymer complex of mercury.

On the other hand,  $\text{Cd}^{2+}$  ions form a complex with QSA, which shows the same composition disregarding the condition in which the synthesis is carried out. The solid complexes are hydrated (after being air dried), with lattice type water, joined to OH and  $\text{SO}_3\text{H}$  ligand groups with the hydrogen bonds. Only in the complex  $\text{Cd}(\text{C}_{15}\text{H}_9\text{O}_{10}\text{S})_2 \cdot 10\text{H}_2\text{O}$ , two molecules of water are bound with the cation of metal and belong to the inner coordination sphere, evidenced by the temperature of water dissociation higher than in the case of lead complexes. The acquired complexes are sparingly soluble in water, both at 20°C and 36°C; their solubility range is  $10^{-3}$ – $10^{-4}$  M (Table 4).

**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 (Table 1) seem to indicate that the compounds are subject to gradual decomposition with a rise in temperature. The occurrence of the first and second endothermal effects (DTA curve) is due to the separation of crystallization water in the temperature range of 20°C to 200°C. The highest dehydration temperature is observed for the  $\text{Cd}(\text{C}_{15}\text{H}_9\text{O}_{10}\text{S})_2 \cdot 10\text{H}_2\text{O}$  complex, which suggests that part of water is directly connected with the metal in the inner, coordination sphere. Further decomposition of the compounds (200°C–900°C) is complex (effects overlap). It is related with the separation of constitutional water and burning coal and sulfur down to oxides. Above 600°C, the final decomposition products, oxides and sulfates(VI) of the appropriate metal were formed.

**Mass spectra:** The ESI and LSI mass spectra confirm the suggested structure of the complexes. The peaks related to the molar mass of the compounds and their structural fragments are listed in Table 2. In the spectrum of each of the complexes studied

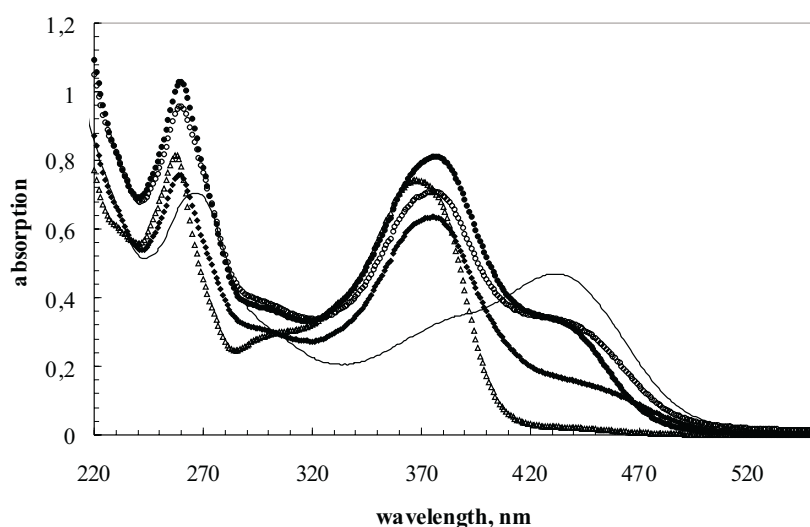
there appeared a peak related to the free ligand (or its dimer). Lack of peaks of the complexes in the ESI spectrum of the complexes of lead(II) with QSA may result from low solubility of the compounds under the determination conditions. In spectra acquired with LSI technique, fragmentation ions were detected that formed by breaking the following bonds [8]:

Broken bonds	Structural element of flavone contained in the fragmentation ion	m/z	Fragment determination	Pattern of flavone molecule decomposition
9C–1O 4C–10C	ring A ring B	109.0 192.3	<b>F 1</b> <b>F 2</b>	
2C–1O 3C–4C	ring A	151.0	<b>F 3</b>	
2C–1O 4C–10C	ring B	258.9	<b>F 4</b>	

In the Cd-QSA spectrum there is an m/z 751.4 ion corresponding to a particle composed of Cd<sup>2+</sup> ion bound with QSA and fragment F4, which contains 3OH and 4CO groups; it is the evidence for the metal ion being bound by this group in a ligand particle.

**Electronic spectra:** UV-VIS spectra of the investigated complexes were taken in methanol. QSA in methanol has two  $\pi \rightarrow \pi^*$  intensive absorption transfer bands (258 and 368 nm), whereas in the spectra of the Cd(C<sub>15</sub>H<sub>9</sub>O<sub>10</sub>S)<sub>2</sub> · 10H<sub>2</sub>O, Hg(C<sub>15</sub>H<sub>9</sub>O<sub>10</sub>S)<sub>2</sub> · 8H<sub>2</sub>O and Pb(C<sub>15</sub>H<sub>9</sub>O<sub>10</sub>S)<sub>2</sub> · 8H<sub>2</sub>O complexes besides  $\pi \rightarrow \pi^*$  bands (259 i 376 nm) there also appears a new band in the visible range at  $\lambda = 425\text{--}430$  nm (Fig. 2). The band is related to the charge-transfer L→M. The similarity shown by the absorption electronic spectra of the compounds suggests their similar structure. In the spectrum of the Pb(C<sub>15</sub>H<sub>8</sub>O<sub>10</sub>S) · 4H<sub>2</sub>O complex (obtained at an excess of lead(II) ions) there may be observed a  $\pi \rightarrow \pi^*$  band shift in the ultraviolet range from 258 to 267 nm and from 368 to 386 nm and a considerable decrease in the intensity of the second  $\pi \rightarrow \pi^*$  band. Besides, in the spectrum there is an intensive charge-transfer band at about 430 nm (Fig. 2). This fact suggests that a metal cation–ligand bond may be different from those in the other complexes.

**Infrared spectra:** In order to determine the structure of the obtained complexes, their infrared spectra were taken. Table 3 presents the band frequencies of >C=O and SO<sub>2</sub> groups in the complexes; for comparison, the frequencies of those bands for quercetin, QSA and sodium salt QSA (NaQSA) are also given. While analysing IR spec-



**Figure 2.** Absorption spectra in visible and ultraviolet ranges of methanol solutions: QSA ( $\Delta$ ,  $c = 4.23 \cdot 10^{-5}$  M),  $\text{Cd}(\text{C}_{15}\text{H}_9\text{O}_{10}\text{S})_2 \cdot 10\text{H}_2\text{O}$  ( $\bullet$ ,  $c = 2.11 \cdot 10^{-5}$  M),  $\text{Hg}(\text{C}_{15}\text{H}_9\text{O}_{10}\text{S})_2 \cdot 8\text{H}_2\text{O}$  ( $\blacklozenge$ , saturated solution),  $\text{Pb}(\text{C}_{15}\text{H}_9\text{O}_{10}\text{S})_2 \cdot 8\text{H}_2\text{O}$  ( $\circ$ , saturated solution),  $\text{Pb}(\text{C}_{15}\text{H}_8\text{O}_{10}\text{S}) \cdot 4\text{H}_2\text{O}$  ( $-$ , saturated solution).

tra and the frequency values of the  $>\text{C}=\text{O}$  group, one can observe, in QSA, a shift of this band towards lower frequencies ( $1640 \text{ cm}^{-1}$ ) in relation to the position of that band in quercetin ( $1673 \text{ cm}^{-1}$ ). The shift is probably due to the weakening of the carbonyl bond by the intermolecular hydrogen bond, which is being formed, with the strongly acidic hydrogen of the sulfonic group [9]. In NaQSA, sodium bound in the sulfonic group does not directly interact with the  $>\text{C}=\text{O}$  group, hence the oscillation frequency of the carbonyl group in the NaQSA is  $1665 \text{ cm}^{-1}$  and approaches the value observed in quercetin ( $1673 \text{ cm}^{-1}$ ). In complexes with metals, the band of the  $>\text{C}=\text{O}$  group occurs at the frequencies  $1652\text{--}1656 \text{ cm}^{-1}$ , and is shifted, on average, by  $14 \text{ cm}^{-1}$  towards higher values in comparison with QSA. It is the evidence of metal cation binding with the carbonyl group. The sulfonic group band occurring at  $1178 \text{ cm}^{-1}$  in QSA in the complexes shifts to about  $1180 \text{ cm}^{-1}$ , which is connected with the change in the neighbourhood of the group in the complexes. The spectra of the complexes of Cd(II), Hg(II) and Pb(II) (lead complex synthesized at an excess of the ligand) show great similarity, which suggests their similar structure. They form five-membered chelates through 3OH and 4CO groups. It is indicated by the shift of the  $>\text{C}=\text{O}$  group band in the complexes towards higher frequencies in relation to the  $>\text{C}=\text{O}$  band in the ligand. If the metal cation occupies a position at 5OH and 4CO groups and six-membered chelates are formed as in the complexes of the sulfonic derivative of chryzin (5,7-dihydroxyflavone) [10,11], then the carbonyl group band occurs at  $1636\text{--}1637 \text{ cm}^{-1}$ . In paper [12] it was also found that QSA binds with metal cations through 3OH and 4CO groups.



The infrared spectrum of the complex of lead(II) with QSA at an excess of the metal ( $\text{Pb}(\text{C}_{15}\text{H}_8\text{O}_{10}\text{S}) \cdot 4\text{H}_2\text{O}$ ) shows a considerable band broadening in the range 2000–3500  $\text{cm}^{-1}$  in relation to the rest of investigated compounds. In this range there appear stretching vibration bands of hydroxyl groups bound with intermolecular hydrogen bonds [13]. In the complex under investigation the observed change may result from a simultaneous replacement of hydrogen atoms with a metal cation in two hydroxyl groups: in positions 3 and 5. Then appears a chelate complex with two five- and six-membered rings. It was found in paper [14] on the investigation of complexation in solutions of the Zr(IV), Sb(III) ions with the flavonoids that at an excess of  $\text{Zr}^{4+}$  ions in relation to flavonoids, which have 3OH, 4CO and 5OH, 4CO groups, in acid medium, the metal interacts simultaneously with 3OH, 5OH and 4CO groups. Then a considerable bathochromic shift of the ligand band is observed in the visible light range (about 80 nm for the complex with quercetin). The data suggest attaching the lead ion simultaneously at 3OH, 5OH and 4CO positions.

### CONCLUSIONS

The reactions of Cd(II), Hg(II) and Pb(II) ions with QSA in aqueous solutions at pH 1.3–1.7 lead to the precipitation of chelate complexes sparingly soluble in water. The composition of the complexes depends on the conditions of the synthesis and the kind of metal ion:  $\text{Cd}^{2+}$  ions form  $\text{Cd}(\text{C}_{15}\text{H}_9\text{O}_{10}\text{S})_2 \cdot 10\text{H}_2\text{O}$  compound disregarding the conditions;  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  ions precipitate as  $\text{M}(\text{C}_{15}\text{H}_9\text{O}_{10}\text{S})_2 \cdot 8\text{H}_2\text{O}$  (where  $\text{M} = \text{Hg}^{2+}, \text{Pb}^{2+}$ ) at an excess of ligand; an excess of  $\text{Pb}^{2+}$  ions leads to the formation of  $\text{Pb}(\text{C}_{15}\text{H}_8\text{O}_{10}\text{S}) \cdot 4\text{H}_2\text{O}$ . On the basis of UV-VIS, IR, ESI MS and LSI MS analyses the site of metal ion addition to QSA molecule was proposed. Formation of sparingly soluble complex compounds of QSA with Cd(II), Hg(II) and Pb(II) ions suggests that non-toxic QSA could be an antidote against above mentioned metals.

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