

New Complexes of La(III), Ce(III), Tm(III), Yb(III) and Lu(III) with Quercetin-5'-sulfonic Acid

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New solid complexes of La(III), Ce(III), Tm(III), Yb(III) and Lu(III) with quercetin-5'-sulfonic acid at pH 1.4–1.5 were obtained. On the basis of the elementary analysis and thermogravimetric investigation, the following composition of the compounds was determined: $\text{Ln}(\text{C}_{15}\text{H}_9\text{O}_{10}\text{S})_3 \cdot n\text{H}_2\text{O}$ ($n = 14\text{H}_2\text{O} - \text{La, Ce}$; $n = 13\text{H}_2\text{O} - \text{Tm, Yb, Lu}$). UV and VIS suggest that complexes of CT type were acquired. IR spectra and magnetic and thermogravimetric investigations demonstrate that the obtained complexes are hexa-coordinated. Groups 3OH and 4CO of the ligand participate in binding Ln(III).

Key words: complexes, quercetin-5'-sulfonic acid, lanthanides, thermogravimetric analysis, spectroscopic properties, magnetic properties

Previously [1,2], complexes of the Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III) and Er(III) ions with QSA, a sulfonic derivative of quercetin, (Fig. 1), were synthesized and examined. In [3], QSA was applied as a new reagent to the spectrophotometric determination of lanthanides. Some compounds of lanthanides with quercetin and QSA show strong luminescence and can therefore be used in laser technology [4,5]. The authors of [6,7] demonstrated that quercetin and its complexes with metals interact with DNA. They investigated the effect of these compounds on cancerous cells in the human organism (the study involved blood, the colon, the lungs, the stomach, the liver and the prostate). The results indicate that although quercetin itself does not show therapeutic properties (blood cancer),

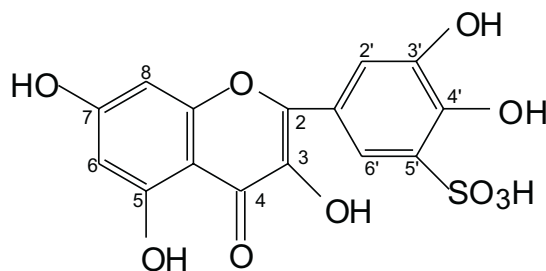


Figure 1. Structure of quercetin-5'-sulfonic acid particle (QSA).

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its complexes have such properties, especially the europium complex. The antioxidant properties of the above compounds were examined and it was found that the gadolinium complex seems to possess the strongest antioxidant activity. Since QSA is a compound which is absolutely non-toxic and, unlike quercetin, well soluble in water, it seems reasonable to look for new flavonoid-metal complexes of interesting properties, which may find their application in cancer therapy or as potential laser materials.

This paper is a continuation of the research on complexes of QSA with lanthanides, in which the structure of the complexes of La(III), Ce(III), Tm(III), Yb(III) and Lu(III) with QSA is more thoroughly discussed, based on IR spectra and the enthalpy values of the dehydration reaction of the complexes.

EXPERIMENTAL

Reagents: QSA was obtained by the method described in paper [8]. 0.1 mole/dm³ solutions of lanthanum(III) and cerium(III) nitrates(V) were obtained by dissolving the appropriate weighed amounts of the salts in redistilled water. 0.1 mole/dm³ solutions of thulium(III), terbium(III) and lutetium(III) chlorides were obtained by hot dissolution of the appropriate weighed amounts of Tm₂O₃, Yb₂O₃ and Lu₂O₃ oxides in concentrated hydrochloric acid ($d = 1.19 \text{ g/cm}^3$). The excess of the acid was evaporated and the rest dissolved in redistilled water. All the reagents were analytically pure.

Synthesis of the complexes: 100 cm³ of a hot QSA solution containing 0.05 mole of the substance was added to the same volume of solution containing 0.1 mole of the appropriate lanthanide ions. pH of the mixture was 1.4–1.6. The spongy, yellow-green deposits, which precipitated after about half an hour, were, after a few hours, filtered off and washed few times with redistilled water. The obtained deposits, after being dried in air and then broken up, were yellow except the Ce(III) complex, which was yellow-green.

Analysis: The contents of C, H and S in the investigated compounds were determined with a Carbo-Erba EA-1108 apparatus for elementary microanalysis. The metal content was determined spectrophotometrically with Arsenazo I for La(III) and Ce(III) [9] and xylenole orange for Tm(III), Yb(III) and Lu(III) [10]. The water content in the complexes was determined by gravimetric and thermoponderal methods. The results of the analyses confirm the following composition of the compounds obtained: Ln(C₁₅H₉O₁₀S)₃·nH₂O, where: Ln – lanthanide(III) ion, n = 14H₂O for La and Ce; n = 13H₂O for Tm, Yb and Lu.

Thermogravimetric analysis: Thermal examination of the samples was carried out with a Setsys TG-DSC 15 apparatus between 20–1000°C in normal atmosphere. A 10 mg sample was heated at a speed of 10°C·min⁻¹. The results were TG curves representing mass losses and DTG – differential derivative of TG and HeatFlow (J·g⁻¹) curves, showing phase changes. Table 1 lists the thermal investigation results: mass losses in particular samples (TG) in temperature intervals, enthalpies of the particular phase transformations (HeatFlow and its differential derivative dHeatFlow) of QSA and its complexes with La(III), Ce(III), Tm(III), Yb(III) and Lu(III) ions.

Spectral measurements: The UV-VIS spectra of the complexes in ethanol were recorded using a Specord UV-VIS (Carl Zeiss Jena) and Beckman DU 640 spectrophotometers. Fig. 2 shows the electronic absorption spectra of the examined complexes. IR spectra within the range 4000–500 cm⁻¹ were made in KBr pellets by means of an FT-IR Paragon 1000 spectrophotometer (Perkin-Elmer).

Magnetic measurements: Measurements of magnetic susceptibility of the complexes were made with a Quantum Design SQUID magnetometer (type MPMS-5) in the temperature range from –275 to 27°C. The effective magnetic moments were calculated using the formula: $\mu_{\text{ef}} = 2.83(\chi_M \cdot T)^{1/2}$ B.M., where: χ_M – magnetic susceptibility of the appropriate lanthanide with an allowance for diamagnetism [11], T – temperature in K. The values of effective magnetic moments are listed in Table 2.

Table 1. Results of thermogravimetric analysis of lanthanide complexes with QSA.

Air atmosphere	Decomposition Stage									Final decomposition product	
	First	Second	Third	Fourth	Fifth	Sixth	Seventh	Eight	Ninth		
QSA · 4H ₂ O											
Temperature interval (°C)	23–170	170–305	305–374	374–567	567–804	804–889	889–985				–
Mass losses (TG, DTG)	15.74%	7.40%	19.99%	53.90%	0.73%	1.93%	0.31%				
Heatflow:											
– peak (°C)	106	–	352	506	–	–	–				
– onset (°C)	77	–	342	374	–	–	–				
– offset (°C)	128	–	361	555	–	–	–				
– enthalpy (J · g ⁻¹)	218.0(endo)	–	221.4(endo)	–6466.0(exo)	–	–	–				
– enthalpy (kJ · mol ⁻¹)	99.0	–	–	–	–	–	–				
La–(QSA) ₃ · 14H ₂ O											
Temperature interval (°C)	25–273	273–350	350–406	406–544	544–674	674–825	855–984				La ₂ (SO ₃) ₃
Mass losses (TG, DTG)	17.58%	7.49%	16.16%	36.86%	5.14%	0%	1.59%				
Heatflow:											
– peak (°C)	97	–	478	–	629	–	–				
– onset (°C)	57	–	415	–	605	–	–				
– offset (°C)	144	–	502	–	653	–	–				
– enthalpy (J · g ⁻¹)	152.2(endo)	–	–7991.0(exo)	–	–644.1(exo)	–	–				
– enthalpy (kJ · mol ⁻¹)	234.0	–	–	–	–	–	–				
Ce–(QSA) ₃ · 14H ₂ O											
Temperature interval (°C)	25–276	276–333	333–380	380–547	547–720	720–800	800–984				Ce ₂ (SO ₃) ₃
Mass losses (TG, DTG)	16.34%	4.85%	12.31%	42.27%	0.26%	1.53%	2.56%				
Heatflow:											
– peak (°C)	100	–	476	–	–	782	–				
– onset (°C)	60	–	390	–	–	751	–				
– offset (°C)	147	–	496	–	–	792	–				
– enthalpy (J · g ⁻¹)	150.4(endo)	–	–9112.9(exo)	–	–	120.8(endo)	–				
– enthalpy (kJ · mol ⁻¹)	231.0	–	–	–	–	–	–				

Table 1. Continue.

Tm-(QSA) ₃ ·13H ₂ O										Tm ₂ O ₃
Temperature interval (°C)	23–254	254–336	336–417	417–525	525–617	617–662	662–800	800–881	881–984	
Mass losses (TG, DTG)	15.66%	6.69%	39.05%	27.12%	2.84%	0.80%	0.73%	1.59%	0.70%	
Heatflow:										
– peak (°C)	117	–	403	and 448	588	–	–	–	–	
– onset (°C)	78	–		355	562	–	–	–	–	
– offset (°C)	169	–		484	609	–	–	–	–	
– enthalpy (J·g ⁻¹)	178.9(endo)	–		–8249.2(exo)	–338.0(exo)	–	–	–	–	
– enthalpy (kJ·mol ⁻¹)	277.0	–				–	–	–	–	
Yb-(QSA) ₃ ·13H ₂ O										
Temperature interval (°C)	23–257	257–339	339–417	417–523	523–623	623–669	669–790	790–889	889–984	
Mass losses (TG, DTG)	15.16%	7.03%	35.42%	26.88%	3.08%	0.72%	0.74%	1.68%	1.13%	
Heatflow:										
– peak (°C)	115	–	403	and 449	590	–	–	–	–	
– onset (°C)	73	–		356	567	–	–	–	–	
– offset (°C)	167	–		484	620	–	–	–	–	
– enthalpy (J·g ⁻¹)	175.5(endo)	–		–7954.4(exo)	–388.3(exo)	–	–	–	–	
– enthalpy (kJ·mol ⁻¹)	272.0	–				–	–	–	–	
Lu-(QSA) ₃ ·13H ₂ O										Lu ₂ O ₃
Temperature interval (°C)	23–261	261–342	342–424	424–544	544–630	630–680	680–775	775–919	919–984	
Mass losses (TG, DTG)	15.12%	7.48%	32.72%	27.80%	4.18%	0.44%	0.44%	2.55%	1.67%	
Heatflow:										
– peak (°C)	106	–	407	and 457	593	–	–	–	–	
– onset (°C)	77	–		360	571	–	–	–	–	
– offset (°C)	128	–		499	609	–	–	–	–	
– enthalpy (J·g ⁻¹)	218.0(endo)	–		–7531.9(exo)	–618.0(exo)	–	–	–	–	
– enthalpy (kJ·mol ⁻¹)	339.0	–				–	–	–	–	

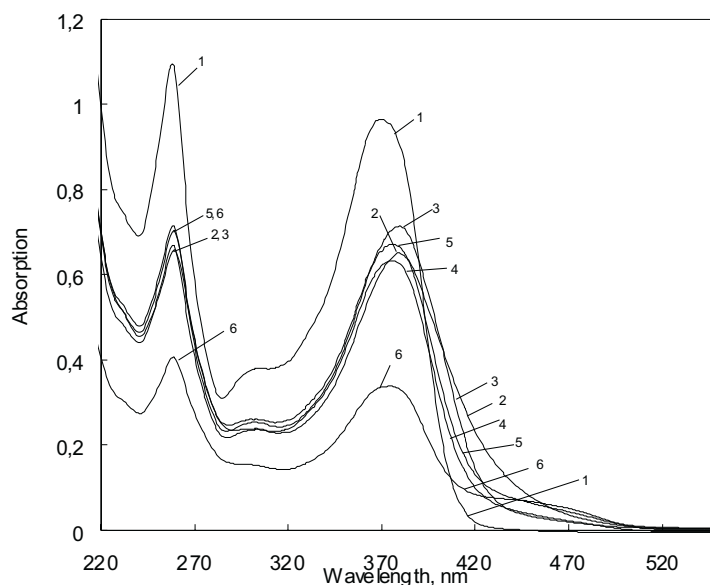


Figure 2. Electronic absorption spectra of QSA and its complexes with lanthanide ions in ethanol: 1 – QSA, 2 – La(III), 3 – Ce(III), 4 – Tm(III), 5 – Yb(III), 6 – Lu(III). Concentrations of solutions: curve 1 – $4.4 \cdot 10^{-5}$ mole/dm³, curves 2–6 – $9.7 \cdot 10^{-5}$ mole/dm³, $l = 1$ cm, reference – C₂H₅OH.

Table 2. Values of effective magnetic moments (μ_{ef}) of the complexes of lanthanide ions with QSA.

Investigated compound	Magnetic moment, μ_{ef} [B.M.]	
	theoretical values (for Ln ³⁺ ions)	values obtained (temp. 293 K)
La(C ₁₅ H ₉ O ₁₀ S) ₃ · 14H ₂ O	0	0
Ce(C ₁₅ H ₉ O ₁₀ S) ₃ · 14H ₂ O	2.55	2.58
Tm(C ₁₅ H ₉ O ₁₀ S) ₃ · 13H ₂ O	7.58	7.10
Yb(C ₁₅ H ₉ O ₁₀ S) ₃ · 13H ₂ O	4.52	4.06
Lu(C ₁₅ H ₉ O ₁₀ S) ₃ · 13H ₂ O	0	0.17

RESULTS AND DISCUSSION

Synthesis of the complexes of La(III), Ce(III), Tm(III), Yb(III) and Lu(III) ions with QSA: QSA of the molecular formula C₁₅H₁₀O₁₀S · 4H₂O, La(III) and Ce(III) nitrates(V) and Tm(III), Yb(III) and Lu(III) chlorides were used for the synthesis of the complexes. QSA was obtained by the sulfonation of quercetin at 80°C; the purity of the compound was checked by paper chromatography [2]. The synthesis of the complexes was carried out in aqueous solutions at mole concentration of the compounds $c_{\text{M}}:c_{\text{QSA}} = 2:1$ at pH 1.4–1.6. The complexes obtained have

the formula $M(C_{15}H_9O_{10}S)_3 \cdot nH_2O$, where M – lanthanide cation, $n = 14$ for La(III) and Ce(III); $n = 13$ for Tm(III), Yb(III) and Lu(III). The compounds are yellow of amorphous sediment structure, the Ce(III) complex is yellow-green. They are hardly soluble in methanol and ethanol, better soluble in DMSO and insoluble in water.

Thermogravimetric analysis: Thermal analysis of quercetin-5'-sulfonic acid (Table 1) indicates that it undergoes six-stage mass changes (TG and DTG curves), between 20–1000°C, accompanied by phase transformations and the carbonization effect (HeatFlow curve). The first effect, in the 23–170°C temperature range, with a 15.74% mass loss, reflected by an endothermic effect (enthalpy $218 \text{ J} \cdot \text{g}^{-1}$) on the HeatFlow curve, is connected with the lost of four water molecules. The second stage (170–305°C) proceeds with a 7.40% mass loss with no changes on the HeatFlow curve. The third, abrupt stage of mass loss is 19.99%, in the 305–374°C temperature range (curves TG and DTG). The effect is connected with endothermic change, marked on the HeatFlow curve, with enthalpy $221.4 \text{ J} \cdot \text{g}^{-1}$. Above 374°C an exothermic process of the sample carbonation starts, characterized by a substantial 53.90% mass loss and $-6466 \text{ J} \cdot \text{g}^{-1}$ enthalpy. The process finishes at 567°C. The fifth stage begins above that temperature and extends up to 804°C. At that stage a small 0.73% mass loss occurs and there are no simultaneous changes on the HeatFlow curve. The sixth stage of thermal changes can be observed between 804–889°C, with a 1.93% mass loss and no changes on the HeatFlow curve. The process of the thermal changes of the investigated sample ends on stage seven in 889–985°C, with an 0.31% mass loss, also with no change on the HeatFlow curve. The results of the thermal analysis for the particular complexes (Table 1) of QSA with lanthanide ions are the direct evidence of the fact that those compounds also undergo multi-stage changes. The common feature of these changes is first the endothermic effect between 25–276°C. This process corresponding to separation of H_2O and the range is much larger than that observed in the case of QSA (23–170°C). This fact suggests that part of the water molecules may be directly connected with the metal. The enthalpy values of these changes are: 152.2; 150.4; 178.9; 175.5; $218.0 \text{ J} \cdot \text{g}^{-1}$ for the complexes of La(III), Ce(III), Tm(III), Yb(III) and Lu(III), respectively. The two further stages of the thermal change are due to the loss of function groups or the destabilization of the complex structure. The changes are accompanied by small mass losses (TG curves), whereas on the HeatFlow curve great exothermic effects (in 273–544°C) occur with enthalpies -7991.0 ; $-9112.9 \text{ J} \cdot \text{g}^{-1}$ for the complexes with La(III) and Ce(III), respectively. Above 540°C, another three-stage transformation, connected with slight mass losses, begins. Above 984°C lanthanum and cerium occur as sulfates(IV): $La_2(SO)_3$ and $Ce_2(SO)_3$. A thermal analysis of the complexes of Tm(III), Yb(III) and Lu(III) with QSA demonstrated that those compounds, unlike those described above, undergo nine-stage thermal changes (Table 1). The first and the second stages are similar to the previous ones: QSA and complexes with La and Ce. The next two stages, the third and the fourth, are characterized by a thermal change and big mass losses. The calculated enthalpy of the phase changes of both the third and fourth stages decreases with the increase in the atomic mass of the lanthanides: -8249.2 ;

–7954.4; –7531.9 J·g⁻¹ for the Tm–QSA, Yb–QSA and Lu–QSA complexes. The fifth stage is related with exothermic change of increasing enthalpy values: –338.0 (Tm–QSA), –388.3 (Yb–QSA), –618.0 (Lu–QSA) J·g⁻¹. Above 620°C, further slight mass losses are observed, which suggests a structural change within the newly formed metal oxides. The final stage is the formation of oxides Tm₂O₃, Yb₂O₃ and Lu₂O₃. The thermolysis of the complexes of the trivalent La, Ce, Tm, Yb and Lu ions with QSA can be elucidated by the atomic mass differences (initial and final lanthanides), as well as by the contraction differences of their ion radius, which may significantly affect the thermolysis process. The investigation carried out in this paper (thermolysis) confirms the periodic nature of different lanthanide characteristics, which are regarded as functions of the atomic number or ion radius.

Electronic spectra: Electronic absorption spectra of the ethanol solutions of the complexes (Fig. 2) exhibit two bands of ligand origin, situated at 259 and 378 nm ($\pi \rightarrow \pi^*$) and a charge-transfer L → M band (inflexion) at about 440 nm. The band is the most conspicuous in the Lu(III)–QSA complex spectrum. In the QSA spectrum there are two bands; $\pi \rightarrow \pi^*$ at 368 nm (band I) and 258 nm (band II). In the spectra of the complexes band I shows a bathochromic 10 nm shift and band II moves for 2–3 nm. Furthermore, the mole absorption coefficients of the $\pi \rightarrow \pi^*$ bands of the complexes and QSA differ considerably; in the complexes the mole values of the band absorption coefficients increase three times in relation to QSA. However, no inner 4f-5d or f-f type transfers, due to the ligand band overlap, can be observed.

Infrared spectra; The IR spectra of the complexes in the range 4000–500 cm⁻¹ show a great similarity, which means that the studied complexes have similar structures. Table 3 presents vibration frequencies of >C=O and SO₃H groups in the complexes. For comparison the frequencies of those bands for QSA were also given. Analysing IR spectra and the vibration frequency values of the >C=O group, it may be observed that in lanthanide complexes the band shifts towards higher frequencies (1653 cm⁻¹) in relation to the vibration frequency of this band in QSA, which appears at 1640 cm⁻¹. In quercetin the vibration frequency of this band occurs at 1672 cm⁻¹, and in QSA, due to a strong intermolecular interaction of the strongly acidic sulfo group proton with the carbonyl group, the frequency of the >C=O band drops to 1640 cm⁻¹ [12]. However, the band of the sulfo group, which in QSA appears at 1179 cm⁻¹, remains practically unchanged in the complexes with frequency 1178 cm⁻¹. In the IR spectrum of QSA, the 1550 cm⁻¹ vibration frequency band, which is due to the presence of the chelate ring formed by the bond >C=O ··· H–O– [13,14], undergoes a shift to 1560–1565 cm⁻¹ in the complexes as the proton in the ring has been replaced by the lanthanide cation. These facts suggest that the >C=O group takes part in the lanthanide bond and sends the free electron pair to the empty outer orbitals of the lanthanide ion. These suggestions are confirmed by the electronic spectra of the complexes where, at 420 nm, an L → M charge shift can be observed. The IR spectra of the complexes do not reflect the coordination bonds of water with the central atom due to the fact that the spectra of anhydrous and hydrated complexes are the same.

Table 3. Position of some bands in IR spectra of QSA and its complexes with lanthanide ions.

QSA·4H ₂ O cm ⁻¹	La(QSA) ₃ ·14H ₂ O cm ⁻¹	Ce(QSA) ₃ ·14H ₂ O cm ⁻¹	Tm(QSA) ₃ ·13H ₂ O cm ⁻¹	Yb(QSA) ₃ ·13H ₂ O cm ⁻¹	Lu(QSA) ₃ ·13H ₂ O cm ⁻¹	Type of vibrations
3550–3200	3550–3200	3550–3200	3550–3200	3550–3200	3550–3200	ν_{OH} in molecules containing H ₂ O and –OH groups (hydrogen bonded)
1640	1653	1653	1653	1653	1653	valence band C=O
1550	1560	1561	1564	1565	1565	vibrations of the chelate ring forming group)C=O···H–O
1481	1494	1494	1489	1488	1489	stretching vibrations –C–OH
1179	1178	1178	1178	1178	1178	$\nu_{\text{asym.}}$ SO ₂

However, thermogravimetric investigation suggests that water is present near to the lanthanide cation as the dissociation of water in the complexes takes place at the temperature about 100°C higher than that in the case of QSA, where water is bound by hydrogen bonds with the OH and sulfo groups. However, a big amount of water in a particle (13–14H₂O) may bring about a shift of its separation range towards higher temperatures.

Magnetic moments: Complexes of La(III), Ce(III), Tm(III), Yb(III) and Lu(III) with QSA are paramagnetic. The obtained values of magnetic moments are in good agreement with the number of odd electrons of the appropriate lanthanide ion (Table 2). In the case of lanthanide(III) ions, their magnetic moment is affected by both the resultant spin moment and the resultant orbital moment of the odd electrons. However, the magnetic moment resulting only from spin moments occurs in the case of the ions of f⁰ and f¹⁴ configuration (La and Lu) and then its value equals 0 [15]. The obtained value 0.17 for the magnetic moment of the Lu–QSA complex is within the experimental error.

Structure of the complexes: Trivalent cations of the lanthanides join three QSA molecules to form complexes of Ln(QSA)₃·nH₂O type (Ln³⁺ – lanthanide cation; n = 14 for complexes of La and Ce and n = 13 for complexes of Tm, Yb and Lu). 3OH and 4CO ligand groups participate in binding the metal to form three five-membered chelate rings. It was also found in previous papers [1,2] that the rest of the trivalent lanthanide ions form complexes of similar structure. Another problem is how to explain the presence of water molecules in the inner coordination sphere. It is known that light lanthanides often have coordination number 9 in the complexes and heavy ones have number 8. The paper makes an attempt at finding the coordination number of light and heavy lanthanides in the complexes with QSA based on the dehydration enthalpy values of the complexes studied. The enthalpy values in kJ/mole of the dehydration reaction of QSA and the complexes are: 99.0 (QSA·4H₂O); 234.0 (La(QSA)₃·14H₂O); 231.0 (Ce(QSA)₃·14H₂O); 276.8 (Tm(QSA)₃·13H₂O); 272.2 (Yb(QSA)₃·13H₂O) and 338.6 (Lu(QSA)₃·13H₂O). If the values are calculated for one water molecule in the compounds, the following values can be obtained: 24.8; 16.7; 16.5; 21.3; 20.9 and 26.1 kJ. As it can be seen, enthalpy values of the hydration of one water molecule in QSA and QSA–lanthanide complexes are of the same order, and in complexes they are even lower, which is the evidence of the similar force of binding water molecules in the ligand and in its complexes. Comparing the obtained values with those describing the hydration energy of lanthanides for one water molecule: 379 kJ for Ce³⁺ and 465 kJ for Lu³⁺ [15], it may be said that the dehydration energy values for one water molecule are one order lower. If one or two water molecules were in the inner coordination sphere of the complexes, the obtained dehydration energy value would be far greater. Making a rough energy balance for a cerium complex, which has 14 water molecules and the structure [Ce(QSA)₃(H₂O)₂]·12H₂O, we get: hydration energy of two water molecules: 2·379 = 758 kJ; dehydration energy of twelve water molecules: 12·24.8 = 297.6 kJ (value 24.8 kJ/1H₂O refers to QSA),

together: 1055.6 kJ/mol. The roughly calculated dehydration energy is considerably greater than that for the cerium complex, *i.e.* 231 kJ/mole.

CONCLUSIONS

In aqueous solutions, at pH 1.4–1.6, La(III), Ce(III), Tm(III), Yb(III) and Lu(III) form with QSA solid complexes of the following composition: $\text{Ln}(\text{C}_{15}\text{H}_9\text{O}_{10}\text{S})_3 \cdot n\text{H}_2\text{O}$, where: $\text{Ln} = \text{La}^{3+}$ and Ce^{3+} with $n = 14$ and $\text{Ln} = \text{Tm}^{3+}$, Yb^{3+} and Lu^{3+} with $n = 13$. An analysis of the UV-VIS and IR spectra and thermogravimetric investigation point to a conclusion that metal cation interacts with 4CO and 3OH groups in QSA and water occurring in the complexes is not contained in the outer coordination sphere. It is lattice-type water bound by hydrogen bonds with OH and SO_3H groups in QSA. The coordination number of the lanthanide(III) ions in the obtained complexes equals to 6.

REFERENCES

1. Kopacz M. and Nowak D., *Microchem. J.*, **47**, 338 (1993).
2. Kopacz M. and Nowak D., *Polish J. Chem.*, **74**, 303 (2000).
3. Kopacz M., Bujonek B., Nowak D. and Kopacz S., *Chem. Anal. (Warsaw)*, **46**, 621 (2001).
4. Kopacz M. and Bartetski A., *Koordin. Khim.*, **4**, 1845 (1978).
5. Kopacz M. and Bartetski A., *Koordin. Khim.*, **5**, 367 (1979).
6. Zhou Jing, Wang Liu-fang, Wang Jin-yi and Tang Ning, *J. Inorg. Biochem.*, **83**, 41 (2001).
7. Zhou Jing, Wang Liu-fang, Wang Jin-yi and Tang Ning, *Trans. Met. Chem.*, **26**, 57 (2001).
8. Terpiłowski J., Mańczyk R. and Kopacz M., *Dissert. Pharm. Pharmacol.*, **18**, 643 (1966).
9. Marzenko Z. and Balcerzak M., *Spectrophotometric Methods in Inorganic Analysis*, PWN, Warsaw 1998 (*in Polish*).
10. Prajsnar D., *Chem. Anal.*, **8**, 71 (1966).
11. König E., *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds*, Springer-Verlag, Berlin 1966.
12. Heneczkowski M., Kopacz M., Nowak D. and Kuźniar A., *Acta Poloniae Pharm.-Drug Research*, **58**, 415 (2001).
13. Nakamoto K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, J. Wiley, N.Y. 1986.
14. Kazitsyna L. and Kupletska N., *Spectroscopic Methods of Determining Organic Compounds Structures*, PWN, Warsaw 1974 (*in Polish*).
15. Brzyska W., *Lanthanides and Actinides*, WNT, Warsaw 1996 (*in Polish*).