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OPTICAL PROPERTIES OF LANTHANIDE SQUARATES

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Two types of lanthanide squarate hydrates of formulae $\text{Eu}(\text{C}_4\text{O}_4)(\text{HC}_4\text{O}_4)(\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}$ (compound I) and $[\text{Ln}_2(\text{C}_4\text{O}_4)_3(\text{H}_2\text{O})_8]$, where Ln = Eu and Gd (compound II) were investigated. The optical properties of crystals I and selected spectral data of compound II are reported and confronted with earlier studies of europium complexes type II. Excitation and emission spectra were measured at 77 K. Effect of polymeric structure on spectroscopic properties is considered and correlated with the structural data. Cooperative intrachain interactions between metal ions coupled via squarate anions were pointed and cooperative absorption was recorded. To check the presence of the Eu^{2+} traces, the EPR and γ -irradiation measurements were applied. Raman spectra of the compound II (where Ln = from Sm to Lu) were measured in the range $50\text{--}500\text{ cm}^{-1}$. Positions of the bands were considered in function of ionic radius of lanthanide ion. The above, together with the data from excitation spectra, allows to localize the Ln–O bands. Vibronic components in electronic spectra were elucidated and assigned.

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1. Introduction

Compounds of the squarate anion with many divalent and trivalent metal ions have been investigated, since they seem to have interesting structures and properties [1–5]. Most often they have polymeric structures where squarate group acts as a bridging ligand. This makes possible to study the exchange interactions between metal ions through the extended bridging groups.

During last few years, intense research of these compounds have been undertaken, first of all to study the nature of interactions occurring in polymeric two-dimensional layer structures [1].

The aim of this paper is to explain the differences observed in optical properties of two types of europium compounds, monomeric $\text{Eu}(\text{C}_4\text{O}_4)(\text{HC}_4\text{O}_4)(\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}$ (compound I) and polymeric $[\text{Eu}_2(\text{C}_4\text{O}_4)_3(\text{H}_2\text{O})_8]$ (compound II), basing on the X-ray and electronic structures.

2. Experimental

Two types (I and II) of europium and gadolinium pure and diluted crystals were prepared according to the procedure described in details in [1]. Samples were checked by X-ray method. Absorption spectra were measured on a Cary-Varian 5 spectrophotometer at 293 K. The excitation and emission spectra were recorded at 77 K using a SLM Aminco SPF 500 spectrofluorometer. Raman experiment was performed with a Jeol IRS-S1 double monochromator equipped with photon counting system (cooled GaAs photomultiplier). Argon laser was used as the excitation source ($\lambda = 514.3$ and 488 nm).

3. Results and discussion

Absorption spectra of the compound II in aqueous solution is dominated by the charge transfer (C-T) transition ($\lambda \approx 350$ nm, Fig. 1) of intensity $P_{\text{exp}} = 2.79 \times 10^{-3}$ (Fig. 1). Very weak $f-f$ transitions are located at the slope of the C-T band. In the same figure the absorption spectrum of isomolar solution of squaric acid is shown, where $\pi-\pi^*$ ($A_{1g} \rightarrow E_u$) and $n-\pi^*$ ($A_{1g} \rightarrow E_g$) transitions are pictured.

Fig. 1. Absorption spectra in the range 300–600 nm for: *a* — aqueous solution of $\text{Eu}_2(\text{C}_4\text{O}_4)_3$ ($c = 5 \times 10^{-3}$ M, reference $c_{\text{sq}} = 7.5 \times 10^{-3}$ M, $l = 5$ cm); *b* — squarate solution isomolar with sample *a* (reference H_2O , $l = 5$ cm); *c* — solid sample of compound II.

The broad C-T band overlaps both ${}^7F_0 \rightarrow {}^5L_6$ and ${}^7F_0 \rightarrow {}^5D_2$ transitions; it was also possible to detect the ${}^7F_0 \rightarrow {}^5D_1$ and 5D_0 transitions. In the spectrum of solid compound II the C-T band is placed at the same energy.

Let us now confront this result with the excitation spectra at 77 K (excitation spectra at room temperature using 4.5 W xenon lamp were not detectable) for both compounds. Significant differences in intensities of separated lines, as well as in population of 7F_1 level (the strong ${}^7F_1 \rightarrow {}^5D_1$ transition in compound II) were observed. The meaningful are, however, the changes seen in the UV region, where drastic decrease in ${}^7F_0 \rightarrow {}^5L_6$ transition intensity in compound II was detected, whereas intensity of that transition is dominating in spectrum of compound I. Besides, the ${}^7F_0 \rightarrow {}^5D_0$ transition in compound II is quite well recorded, while for compound I it almost vanishes. These effects registered in excitation spectra could be a result of differences in symmetry of the Eu^{3+} centre in both types of

compounds, but mainly of polymeric structure of compound II (remind that compound I is monomeric). Moreover, the role of C-T transition in emission quenching cannot be neglected.

To analyze the effects of $f-d$ transition of Eu^{2+} ion which influence both emission and excitation spectra, we made an effort to explain whether traces of Eu^{2+} are present in the crystal structure, as it was proposed in [2]. EPR spectra of diluted $(\text{Gd}_x\text{Lu}_{1-x})_2(\text{C}_4\text{O}_4)_3$ and pure compound II were recorded at 77 K. In contradiction to gadolinium compound, neither before nor after γ -irradiation of compound II EPR signal was detected. Thus, traces of Eu^{2+} were excluded.

Since some spectral effects should be caused by both intra- and interchain interactions, the EPR method was also applied to study the intrachain interactions of metal ions linked by squarate anions [6]. Judging from soft electronic structure of ligand, such interactions could occur in polymeric systems. To sensitize the interaction, mixed Nd-Cu squarate crystals were crystallized, in which Cu concentration was lower than that of Nd. Two signals of Cu^{2+} (at 300 K) and Nd^{3+} (at 5 K) disappear at ≈ 70 K. This phenomenon could be explained by the Nd-Cu intrachain interaction, most likely of superexchange type [6]. Interchain interaction of π -coupling can also occur, since squaric anions in neighboring layers are separated by ≈ 3.2 Å, but it needs further investigations. Those ion pairs coupled in polymeric chains can affect optical properties of the system under consideration, and probably influence the crystal colors.

Let us recognize the X-ray data. Compound I (light yellow crystals) is a monomer; environment of Eu^{3+} ion is composed of six water molecules and two oxygen atoms of squaric acids, whereas in compound II (intense yellow crystals) the coordination sphere of metal is formed by four H_2O molecules and four oxygen atoms of bridging bidentate and tridentate squaric acids [1, 3].

While the emission properties depend only on multiphonon process promoted by OII vibration modes, a stronger quenching should be observed in compound I since the energy gaps are comparable.

The differences shown in Figs. 2 and 3 are most probably caused by C-T transitions, which could take place in nonradiative deexcitation. That is why the

Fig. 2. Excitation spectra for the compounds I and II at 77 K.

Fig. 3. Emission spectra of compounds I and II at 77 K.

drastic differences in emission intensities, differences in excitation spectra, as well as temperature dependence of emission quenching are observed. In this type of ligand, the energy transfer to europium should be expected from triplet state of ligand. However, the energy of C-T transition and relatively wide slope of its parabola lead to quenching the emission at room temperature. This situation is changed at 77 K and intensities of emission are much stronger.

In emission spectra, marked differences are observed in luminescence intensities (Fig. 3) and splitting of $^5D_0 \rightarrow ^7F_J$ transitions between compound I (Table I) and polymeric compound II. Therefore the C_{2v} symmetry of Eu^{3+} centre is predicted on the basis of group theory.

Confrontation of $^7F_0 \rightarrow ^5D_2$ transitions (Fig. 2) in the excitation spectra of both compounds demonstrates well how the optical properties are affected by polymeric structure. Besides sharp electronic lines at high energies, a rich set of vibronic components was recorded. Intensities of vibronic components for both

TABLE I

Experimental energy levels values for Eu^{3+} in
 $Eu(HC_4O_4)(C_4O_4)(H_2O)_6 \cdot H_2O$.

Transition	Energy [nm]	Energy [cm ⁻¹]	Transition	Energy [nm]	Energy [cm ⁻¹]
$^5D_0 \rightarrow ^7F_0$	579.9	17244	$^5D_0 \rightarrow ^7F_3$	649.5	15396
$^5D_0 \rightarrow ^7F_1$	591.3	16911		650.3	15377
	592.1	16889		650.0	15384
	594.5	16820		651.8	15342
$^5D_0 \rightarrow ^7F_2$	612.6	16323	653.1	15311	
	616.8	16212	$^5D_0 \rightarrow ^7F_4$	690.0	14492
	618.5	16168		692.0	14450
	619.6	16139		694.2	14405
	696.9	14349		699.9	14287
				701.8	14249

Fig. 4. Raman spectra of compounds I and II in the range 0–800 cm^{-1} .

crystals in the region of internal ligand modes are comparable, but the drastic differences are seen in the range of 0–450 cm^{-1} from 0-phonon lines, where cooperative interaction is considered (Table II). Enhancement of intensities of some lines in the spectrum of compound II ($\approx 330\text{--}350\text{ cm}^{-1}$) is due to cooperative absorption of coupled Eu^{3+} pairs in the polymeric chain, most likely mediated by phonons of energy close to splitting of the ${}^7F_0 \rightarrow {}^7F_1$ level. Moreover, the second line can overlap that mentioned above at 279 cm^{-1} , which remains in resonance with the first Stark component of 7F_1 level (see note of Table II). Cooperative absorption was earlier observed by Buys et al. [7].

TABLE II
Vibronic components in the excitation (${}^7F_0 \rightarrow {}^5D_2$, ${}^7F_0 \rightarrow {}^5D_2$) and luminescence (${}^5D_0 \rightarrow {}^7F_0$) spectra of $\text{Eu}(\text{C}_4\text{O}_4)(\text{HC}_4\text{O}_4)(\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}$ (I) and $\text{Eu}_2(\text{C}_4\text{O}_4)_3(\text{H}_2\text{O})_8$ (II).

Transition	Compound I		Compound II		Assignment ^c
	Energy [nm]	ΔE [cm^{-1}]	Energy [nm]	ΔE [cm^{-1}]	
${}^5D_0 \rightarrow {}^7F_0$	<u>579.9^a</u>		<u>579.7^a</u>		$\delta_{\text{Me-O}}$
(comp. I)	583.3	101	579.2 ^a		
or	584.4	133			
${}^7F_0 \rightarrow {}^5D_0$	585.5	165	574.3	164	
(comp. II)	586.7	200	572.4	222	
			568.9	329	
${}^7F_0 \rightarrow {}^5D_2$	466.9 ^a		467.9 ^a		ν_{10} ν_{11} ν_2 ν_5 ν_9 ν_1
	466.0 ^a		465.9 ^a		
	<u>465.3^a</u>		<u>465.1^a</u>		
	464.7 ^a		464.8 ^a		
	463.2	97	463.1	93	
	460.9	205	461.9	151 279 ^b	
	457.7	357	458.1	329	
	452.6	603	451.9	630	
			451.0	674	
	450.8	691	450.4	700	
	441.8	1133	442.0	1123	
	435.3	1481	435.4	1466	
	432.9	1609	433.7	1560	
	429.2	1808	429.4	1790	

^aElectronic lines; underlined those for which ΔE was calculated.

^b Δ calculated from line 467.9 nm. Energy gaps between 7F_0 and Stark components of 7F_1 for compound II are as follows: 288, 303, 383, 415 and 450 cm^{-1} .

^c Notation as in [8, 9].

TABLE III
Position of Raman bands for lanthanide $\text{Ln}_2(\text{C}_4\text{O}_4)_3(\text{H}_2\text{O})_8$ complexes in the region $0\text{--}500\text{ cm}^{-1}$ as a function of ionic radius of lanthanide ion.

Ln	<i>r</i> [pm]	Frequency [cm^{-1}]							
Lu	97	37	56	71	82	109	120	148	170
		190	240	283	338	360	410	440	
Yb	98	37	56	71	82	109	118	147	168
		189	240	283	335	359	410	440	
Ho	102	36	55	70	80	104	115	144	164
		186	228	280	329	356	404	436	
Dy	103	36	56	70	79	104	114	145	162
		184	226	278	322	352	400	430	
Tb	104	36	56	70	80	103	114	145	161
		183	226	278	321	351	402	428	
Gd	106	37	57	70	80	104	113	143	158
		180	222	275	317	350	395	422	
Eu	107	36	56	70	78	103	111	144	156
		180	220	273	315	347	386	414	
Sm	109	37	57	70	79	103	110	143	155
		178	214	274	311	344	380	415	

Comparison of the electronic spectra with Raman data ($30\text{--}800\text{ cm}^{-1}$) for both types of compounds seems spectacular (Fig. 4). The differences are observed for the b_{2g} symmetry vibrational species of squarate anion (effective in the Jahn-Teller effect) and in the a_{1g} symmetry vibrations, as well as in vibrational mode of MO_8 coordination clusters and lattice phonons. It is not an intention of the authors to perform full vibrational analysis but, basing on available vibrational assignments for $\text{C}_4\text{O}_4^{2-}$ anion [8,9], the vibronic components in electronic transitions are analyzed and listed in Table II. Vibrational frequencies of sample II correspond quite well to those reported by Ribeiro et al. [2].

Note also significant differences in the $200\text{--}400\text{ cm}^{-1}$ range, where complex structure of bands is observed, especially for compound II. Among these lines, basing on careful analysis of Raman spectra of compound II with lanthanides from Sm to Lu, two frequencies between $214\text{--}240\text{ cm}^{-1}$ and $311\text{--}338\text{ cm}^{-1}$ (Table III) are the most sensitive to changes in metal ionic radii. It makes possible, together with the analysis of strong vibronic components in excitation spectra, to localize the Eu-O involved modes at 220 and/or 315 (ν) and 156 (δ) cm^{-1} for the compound II.

4. Conclusions

Absorption spectra of europium squarate in aqueous solution show C-T transition with maximum at 350 nm ($P_{\text{exp}} = 2.79 \times 10^{-3}$). It is located at similar

energy as $n \rightarrow \pi^*$ transition of the ligand, and plays an important role in emission properties of the europium ion.

Confrontation of two types of europium squarates allows to point out the role of polymeric structure in emission properties, indicating strong cooperative absorption at ≈ 330 and 280 cm^{-1} . EPR measurements confirm superexchange interaction of ionic pairs coupled in polymeric chain [6]. The EPR and γ -irradiation experiments excluded presence of the traces of Eu^{2+} ions in the structure.

Analysis of the positions of the Raman bands for the series of polymeric lanthanide squarates of formula $\text{Ln}_2(\text{C}_4\text{O}_4)_3(\text{H}_2\text{O})_8$, together with positions of strong vibronic components of excitation spectrum of Eu^{3+} allows to localize the metal-oxygen involved vibrations at 220 and/or $315 (\nu)$ and $156 \text{ cm}^{-1}(\delta)$.

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