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SPECTROSCOPIC PROPERTIES
OF $[\text{Nd}(\text{C}_3\text{H}_7\text{NO})(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$
SINGLE CRYSTAL WITH TENFOLD OXYGEN
COORDINATION Nd^{3+} CENTRE

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The absorption spectra of $[\text{Nd}(\text{C}_3\text{H}_7\text{NO})(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ were measured at 293 K and 5 K and the intensities of $f-f$ transitions were investigated. The electron-phonon features observed in absorption spectra were identified and compared with other available data for Nd systems.

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1. Introduction

Few years ago we reported the results of the intensity analysis for non-aqueous lanthanide nitrate pentahydrate solutions [2]. The hypersensitive transition of unexpected high intensity was observed. It was higher than that observed in lanthanide nitrate melts [3] and anhydrous lanthanide nitrates [4]. The conductivity measurements done at low concentration have shown that the electrolyte was 1:2 [2] and at higher concentration 1:1 [5-7]. They have indicated that there are two nitrate ions involved in the first coordination sphere. The surprisingly high intensity of hypersensitive transition in such system was explained by effect of ligand polarizability mechanism of Mason [8, 9]. The structural aspects of spectroscopic properties of formed solvates were investigated.

2. Experimental

The single crystals were grown from anhydrous dimethylformamide solution of $\text{Nd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. The crystals of good optical quality were checked by X-ray diffraction. The optical measurements were performed using a Cary-Varian-5 spectrophotometer equipped with a helium flow cryostat in the region 320-920 nm. The intensities of optical lines were calculated using ICH program [2] and transformed to the oscillator strength values. The IR spectra were recorded with a Bruker IFS 88 FTIR spectrometer.

3. Results and discussion

Figures 1 and 2 have shown the absorption spectra of neodymium nitrate solvate single crystals at 293 K and 5 K. The structure of absorption bands is very complex and the number of optical lines exceeds the number expected for C_i site symmetry of neodymium ions. Strong lines are accompanied by weak sidebands at higher energy; mainly those which correspond to the transitions obeying the selection rule $|\Delta J| = 0, 2$. They are of vibronic origin. The optical line of ${}^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition is a narrow and sharp singlet line (3 cm^{-1}), indicating the presence of one site of Nd^{3+} ion in the crystal. Judging from the rather long Ln-Ln distances [1], the cooperative interaction can be neglected.

Analysis of the optical lines observed for the ${}^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}$ transitions is presented in Table I. Besides main relatively intense electronic lines, one can find the vibronic components whose energies correspond to Me-O vibronic motions, while other lines are due to coupling with nitrate and C=O vibrations. In Table I there are presented only those lines which are repeated for all Stark components of given electronic transition.

The essential crystal structure data of $[\text{Nd}(\text{C}_3\text{H}_7\text{NO})(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ compound are compiled in Table II [1]. Neodymium ion occupies a ten-coordinated position in the crystal with the shortest Me-O-C bonding length of amide molecules. The mean value of Me-O(H_2O) is 2.462 \AA and of Me-O(NO_3^-) is 2.601 \AA . Judging from the short Me-O(-C) distance, these vibronic components should be the most intense. Since the analysis of intensity of vibronic components for Nd^{3+} ions is rather difficult, we were not able to elucidate the intensity given by particular vibronic coupling. The analyses for the tenfold europium and terbium nitrates hexahydrate similar to ours were made by Blasse et al. [10] and by Moret et al. [11]. They found the coupling between an electronic transition on a lanthanide ion and the Me-O and NO_3^- vibrations in a neighbouring molecular ion (at frequency $\nu_{\text{Me-O}} \approx 150 \text{ cm}^{-1}$, $\nu_{4\text{NO}_3^-} \approx 730\text{--}740 \text{ cm}^{-1}$). However, in our case, because of the amide inner-sphere coordination, the distortion of BCSAP polyhedron is significant and the Me-O distances vary much more compared to the twelve-coordinated Ln^{3+} ions in lanthanide magnesium nitrate hydrates with almost S_6 site symmetry [12] or in anhydrous lanthanide nitrates [4]. It leads to much more complex IR spectrum and consequently to more complex vibronic spectrum (Figs. 2, 3).

The comparison of intensities ($P \times 10^8$) in the spectrum of the title compound and those of the original and diluted solutions is presented in Table III. The intensities of the hypersensitive transition (${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) in the absorption spectra of $[\text{Nd}(\text{C}_3\text{H}_7\text{NO})(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ single crystal and of solutions indicate existence of at least two forms in equilibrium. The most stable and sparingly soluble species crystallizes as $[\text{Nd}(\text{C}_3\text{H}_7\text{NO})(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$. However, in the original solution the form II is predominant, since the intensity of the ${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition is higher. It can be realized by stronger Me-O(amide) interaction, given by exchange of NO_3^- group by more than one amide molecules. As a consequence, the pseudo-layer structure could be formed, leading to the changes of polarizability.

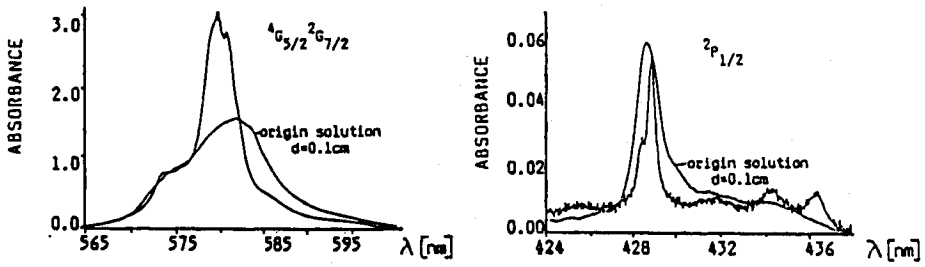


Fig. 1. The absorption spectra of $[\text{Nd}(\text{C}_3\text{H}_7\text{NO})(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ single crystal ($d = 0.029$ cm) and of the original solution ($d = 0.1$ cm) at 293 K.

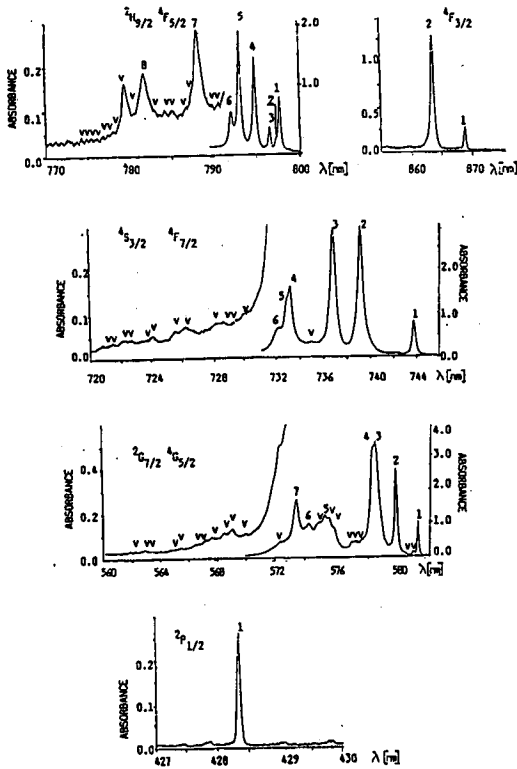


Fig. 2. The absorption spectra of $[\text{Nd}(\text{C}_3\text{H}_7\text{NO})(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ single crystal at 5 K ($d = 0.027$ cm).

TABLE I

The electronic and vibronic components in absorption spectra of
 $[\text{Nd}(\text{C}_3\text{H}_7\text{NO})(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ ($T = 5 \text{ K}$).

Transition		[cm ⁻¹]			
${}^4I_{9/2} \rightarrow {}^4F_{5/2}$	1	12535			
			+103		} $\nu_{\text{Nd-O}}$
			+111		
			+162		
			+173		
			+216		} $\nu_{\text{Nd-OH}_2}$
			+236		
			+339		} $\rho_{\text{C=O}}$
			+352		
	+361				
${}^4I_{9/2} \rightarrow {}^2H_{9/2}$	1	12545			
		12553			
		12579			
		12606			
		12622			
${}^4I_{9/2} \rightarrow {}^2G_{7/2}$	1	12687			
		12792			
		17206		} $\nu_{\text{Nd-O}}$	
			+118		
			+125		
	+163				
	+170				
	+187	} $\nu_{\text{Nd-OH}_2}$			
	+231				
	+338	} $\rho_{\text{C=O}}$			
	+366				
${}^4I_{9/2} \rightarrow {}^2G_{7/2}$	2	17247			
		17286			
		17291			
		17384			
${}^4I_{9/2} \rightarrow {}^2G_{7/2}$	3	17400			
		17438			

The oscillator strength values of hypersensitive transition in solutions 1 and 2 are comparable, indicating the existence of similar forms in both the solutions.

The temperature dependence of intensity revealed the change of population of sublevels of ${}^4I_{9/2}$ ground state and the vibronic coupling in electronic lines, confirming thus the results obtained in the spectrum at 5 K. The weak satellite lines,

TABLE II
Selected bond lengths [\AA] of $[\text{Nd}(\text{C}_3\text{H}_7\text{NO})(\text{NO}_3)_3(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$.

Nd-O(1w)	2.481(3)	Nd-O(4)	2.614(4)
Nd-O(2w)	2.469(4)	Nd-O(5)	2.575(4)
Nd-O(3w)	2.435(3)	Nd-O(6)	2.557(4)
Nd-O(1)(amid)	2.352(3)	Nd-O(8)	2.601(3)
Nd-O(2)	2.666(4)	Nd-O(9)	2.591(3)
Nd-Nd	6.657		$\div 9.896$

TABLE III
The oscillator strength values of the title compound and solutions.

Compound	Original solution	$[\text{Nd}(\text{C}_3\text{H}_7\text{NO})(\text{NO}_3)_3(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$		$\text{Nd}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$
Form	1	I		II/2
Temperature	293 K	293 K	5 K	293 K
Concentrat.	0.7688 M	4.29 M	4.29 M	0.1013 M
${}^4\text{F}_{3/2}$		208.66	80.69	271.66
${}^4\text{F}_{5/2}$ ${}^2\text{H}_{9/2}$		796.17	360.67	1155.63
${}^4\text{F}_{7/2}$ ${}^4\text{S}_{3/2}$		870.43	601.42	1219.73
${}^4\text{F}_{9/2}$		57.82	54.51	93.91
${}^2\text{H}_{11/2}$		14.79	15.18	24.49
${}^4\text{G}_{5/2}$ ${}^2\text{G}_{7/2}$	3411.82	2145.10	1066.38	3235.84
${}^2\text{K}_{13/2}$ ${}^4\text{G}_{7/2}$	}	745.61	401.65	1134.34
${}^4\text{G}_{9/2}$				
${}^2\text{K}_{15/2}$ ${}^2\text{G}_{9/2}$	}	183.39	172.62	261.12
$({}^2\text{D}, {}^2\text{F})_{3/2}$				
${}^4\text{G}_{11/2}$	}	21.61	11.87	54.79
${}^2\text{P}_{1/2}$ ${}^2\text{D}_{5/2}$				
${}^4\text{D}_{3/2}$ ${}^4\text{D}_{5/2}$	}	776.36	554.18	1320.44
${}^2\text{I}_{11/2}$ ${}^4\text{D}_{1/2}$				
${}^2\text{L}_{15/2}$	}	117.20	241.38	
${}^2\text{I}_{13/2}$ ${}^4\text{D}_{7/2}$				
${}^2\text{L}_{17/2}$				

as mentioned above, can correspond to the Me-O vibration mode in the region $100\text{--}200\text{ cm}^{-1}$, Me-OH₂ stretching mode of the water molecules ($220\text{--}230\text{ cm}^{-1}$) and Me-O-C vibration at $338\text{--}360\text{ cm}^{-1}$ (Figs. 2, 3; Table I).

According to [13, 14], the coupling mechanism is the dipole-dipole interaction, decreasing with distance as R^{-6} . The vibronic intensity is proportional to

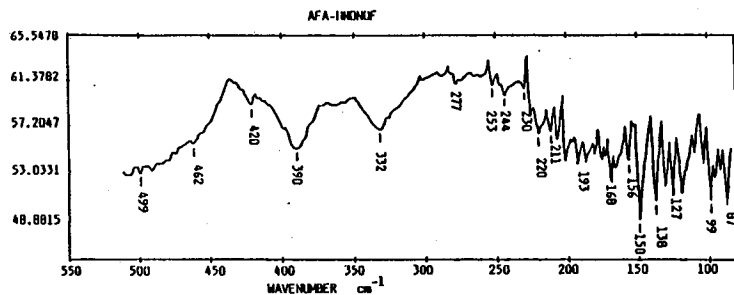


Fig. 3. The IR spectra of $[\text{Nd}(\text{C}_3\text{H}_7\text{NO})(\text{NO}_3)_3(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ single crystal.

the infrared oscillator strength of the vibrational transition involved. Estimation of the intensity given by relevant vibronic coupling needs further investigations of Eu^{3+} , Gd^{3+} , or Pr^{3+} single crystals.

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