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Spectroscopic study of neodymium soaps in 1-pentanol[☆]

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Abstract

The optical absorption spectra of neodymium(III) butanoate, pentanoate, hexanoate, heptanoate and octanoate in 1-pentanol have been measured. This solvent has been chosen, because the neodymium(III) soaps are sufficiently soluble in it. A set of free-ion parameters is obtained by fitting the calculated energy levels against the experimental levels. The experimental dipole strengths of the transitions are determined from the absorption spectra and parameterised in terms of the Judd–Ofelt intensity parameters Ω_λ (λ=2, 4, 6). The Ω_4 values go through a maximum for neodymium(III) hexanoate, whereas the Ω_2 parameter increases in the order butanoate<pentanoate<hexanoate<heptanoate<octanoate. The Ω_6 parameter shows only an increase between the butanoate and the pentanoate complex, whereas this parameter remains fairly constant for the higher homologues of the neodymium(III) soaps.

Keywords: Lanthanides; Rare earths; Optical properties; Spectroscopy; Judd–Ofelt theory; Metal soaps

1. Introduction

The alkali salts of the fatty acids (=carboxylic acids with long alkyl chains) are well known as *soaps*. These soaps are water soluble. If the alkali ion in the higher homologues is replaced by an alkaline earth or by a transition metal ion, the resulting compounds are water insoluble, but more soluble in non-polar organic solvents. The alkaline earth and the transition metal salts of the fatty acids are the so-called *metal soaps* [1,2]. The lanthanides, or the rare earths in general, are also able to form metal soaps. These compounds have the general formula $Ln(C_nH_{2n+1}COO)_3$ [3,4]. Although in the literature several studies on lanthanide soaps in solution can be found, among them Refs. [5–11], hardly any reports on the spectroscopic properties in solution are available [12,13]. A detailed knowledge of the electronic properties of these lanthanide complexes is desirable, because they can have several possible applications, such as catalyst for the polymerisation of 1,4-butadiene (the *cis*-polymer is preferentially formed) [14,15].

In this paper, we describe the spectroscopic properties of neodymium(III) soaps in 1-pentanol. The main aim of this study is to investigate the relation between the chain length of the alkanoate group and the intensities of the f–f transitions. We chose 1-pentanol as the solvent because of the relative good solubility of the neodymium(III) soaps in 1-pentanol. However, since the solubility of the metal soaps is rapidly decreasing with increasing chain length, we restricted ourselves in this study to neodymium(III) soaps with a chain length shorter than nine carbon atoms. The spectra are analysed within the framework of the Judd–Ofelt theory.

2. Experimental details

The neodymium(III) soaps were prepared by a metathesis reaction between neodymium nitrate and the sodium salt of a fatty acid (1:3 molar ratio) in an water/ethanol solution. The precipitate was filtered off, washed with water, ethanol and acetone, subsequently crystallised twice from an toluene/methanol (1:1, v/v) mixture and dried in a vacuum oven for 24 h at 40°C. The crystallised neodymium soaps were filtered off, washed with a little cold methanol and dried for 24 h under vacuum. With the neodymium(III) butanoate, one has to be careful not to use

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too much washing solvent because of the high solubility of this metal soap.

The purity of the soaps was determined by CHN elemental analysis (on a CE Instruments EA-1110 elemental analyser) and by measuring the melting point (on a Mettler-Toledo DSC821e differential scanning calorimeter). We purchased 1-pentanol (99%) from Riedel-de-Haën. Absorption spectra were recorded at room temperature using a Shimadzu UV-3100 spectrophotometer.

3. Results and discussion

The absorption spectra of the neodymium(III) soaps were recorded in 1-pentanol at room temperature. The concentration of the solutions used in this study was 0.01 M. For the higher homologues it proved very difficult to obtain more concentrated solutions at ambient temperature. All the solutions had the typical blue-violet colour of the trivalent neodymium ion [16]. Because of the low concentration of the Nd(III) ion, we used quartz cells with an path length of 10 cm. An advantage of 1-pentanol is its broad spectral window, with a good transparency in the ultraviolet. The adsorption spectrum of neodymium(III) hexanoate in 1-pentanol is shown in Fig. 1.

The energy levels of the trivalent neodymium ion ($4f^3$ configuration) could be determined from the barycentres of the absorption bands [17]. The experimental energy levels are used to extract a set of free-ion parameters. This set of parameters is the start point for the calculated matrix element, necessary for the intensity calculations. The extraction of the free-ion parameters is based on minimising the sum of the squared differences between the experimental and calculated energy levels. For the calculated energy levels, we made use of a parametric free-ion Hamiltonian. The free-ion Hamiltonian is characterised by a set of three electron repulsion parameters (F^2, F^4, F^6), by the spin-orbit coupling constant ζ_{4f}, the Trees configuration interaction parameters (α, β, γ), the three-body configuration interaction parameters (T^2, T^3, T^4, T^6, T^7, T^8) and parameters which describe magnetic interactions (M^0, M^2, M^4, P^2, P^4, P^6). A further parameter E_{AVG} takes into account the kinetic energy of the electrons and their interactions with the nucleus. It shifts only the barycentre of the whole $4f^3$ configuration. So one can write [18,19]:

$$\begin{aligned}H_{\text{free ion}} &= E_{AVG} + \sum_k F^k f_k + \zeta_{4f} A_{SO} + \alpha L(L+1) \\ &\quad + \beta G(G_2) + \gamma G(R_7) + \sum_i T^i t_i + \sum_k P^k p_k \\ &\quad + \sum_l M^l m_l \qquad (1)\end{aligned}$$

where $i = 2, 3, 4, 6, 7, 8$, $k = 2, 4, 6$ and $l = 0, 2, 4$, whereas f_k and A_{SO} represent the angular part of the electrostatic and spin-orbit interaction respectively. L is the total orbital angular momentum. $G(G_2)$ and $G(R_7)$ are the Casimir operators for the groups $G_2$and R_7. The t_i are the three-particle operators. p_k and m_l represent the operators for the magnetic corrections. The starting values of the free-ion parameters were taken from Carnall et al. [20] for $LaF_3:Nd^{3+}$. The parameters E_{AVG}, F^2, F^4, F^6, α, β, γ, ξ_{4f} were freely varied. The other parameters were constraint at

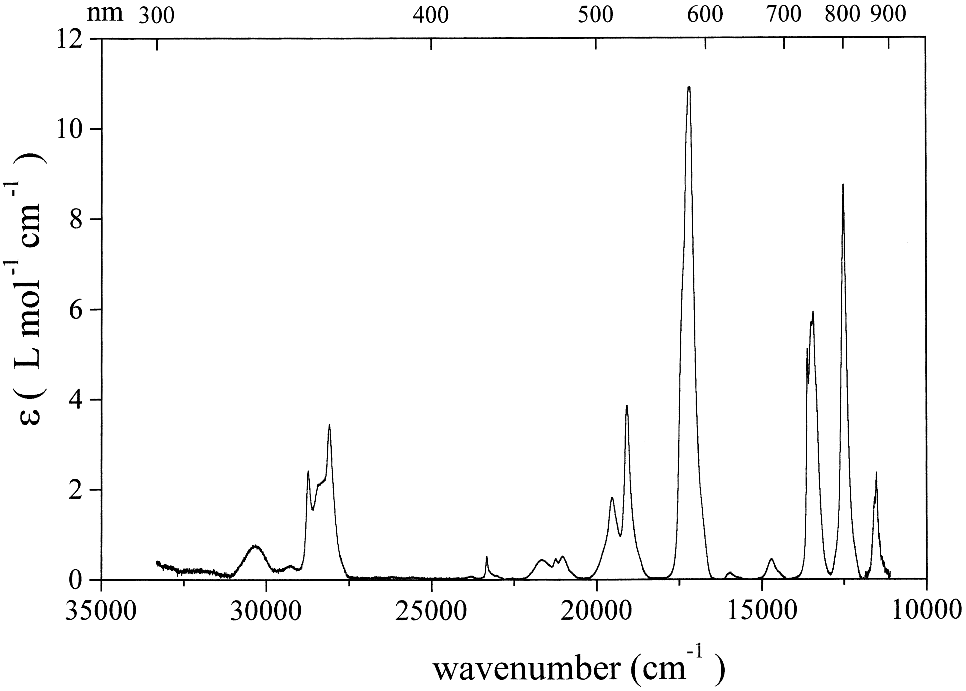

Fig. 1. Absorption spectrum of neodymium(III) hexanoate in 1-pentanol (ambient temperature).

Table 1
Free-ion parameters (in cm^{-1}) of neodymium(III) soaps in 1-pentanol[a]

Parameter	NdC_4	NdC_5	NdC_6	NdC_7	NdC_8
E_{AVG}	24 135±10	24 136±10	24 176±10	24 129±10	24 150±10
F^2	72 364±174	72 308±115	72 454±125	72 308±111	72 522±98
F^4	52 186±380	52 365±378	51 926±414	52 266±366	52 315±323
F^6	35 500±210	35 388±132	35 271±145	35 351±128	35 319±133
α	17.0±1.1	18.1±1.1	16.8±1.1	17.8±1.1	18.4±0.9
β	−591±36	−617±32	−564±34	−607±32	−655±28
γ	1497±55	1519±55	1581±56	1546±53	1600±47
ξ_{4f}	872±6	868±11	870±6	868±5	871±5
T^2	[298]	[298]	[298]	[298]	[298]
T^3	[35]	[35]	[35]	[35]	[35]
T^4	[59]	[59]	[59]	[59]	[59]
T^6	[−285]	[−285]	[−285]	[−285]	[−285]
T^7	[332]	[332]	[332]	[332]	[332]
T^8	[305]	[305]	[305]	[305]	[305]
M^{tot} [b]	[2.11]	[2.11]	[2.11]	[2.11]	[2.11]
P^{tot} [b]	[192]	[192]	[192]	[192]	[192]
σ	38	41	44	39	35

[a] NdC_4, neodymium(III) butanoate; NdC_5, neodymium(III) pentanoate; NdC_6, neodymium(III) hexanoate; NdC_7, neodymium(III) heptanoate; NdC_8, neodymium(III) octanoate. The values in square brackets were constraint during the fitting procedure.

[b] The M^l and P^k parameters were in the following ratios: $M^2/M^0=0.56$, $M^4/M^0=0.38$, $P^4/P^2=0.50$, $P^6/P^2=0.10$.

the values for $LaF_3{:}Nd^{3+}$. The M^l and P^k parameters were in the following ratios: $M^2/M^0=0.56$, $M^4/M^0=0.38$, $P^4/P^2=0.50$, $P^6/P^2=0.10$. In Table 1, the free-ion parameters sets for the Nd(III) alkanoates are given. In Table 2, the experimental and calculated free-ion energy levels of Nd(III) hexanoate are listed.

The transitions observed in the absorption spectra of trivalent lanthanide ions are intraconfigurational f–f transitions. The majority of these transitions are induced electric dipole transitions, although a few magnetic dipole transitions are known. The intensities of the transitions can be characterised by the dipole strength D [21]:

$$D=\frac{1}{108.9Cd}\int\frac{A(\bar{\nu})}{\bar{\nu}}\,d\bar{\nu} \tag{2}$$

where C is the concentration of the neodymium ion ($\mathrm{mol\,l^{-1}}$), d is the optical path length (cm), A is the absorbance ($A=-\log(I_0/I)$) and $\bar{\nu}$ is the wavenumber (cm^{-1}). The dipole strength is expressed in D^2 (Debye^2). According to the Judd–Ofelt theory [22,23], the intensities of induced electric dipole transitions can be described in terms of three phenomenological intensity parameters Ω_λ ($\lambda=2$, 4 and 6):

$$D=\frac{10^{36}}{2J+1}\,\frac{(n^2+2)^2}{9n}\,e^2\sum_{\lambda=2,4,6}\Omega_\lambda|\langle J\|U^{(\lambda)}\|J'\rangle|^2 \tag{3}$$

The factor 10^{36} convert D^2 units into esu·cm. The elementary charge e is 4.803×10^{-10} esu. The degeneracy of the ground state is equal to $2J+1$ (i.e. 10 for Nd^{3+}). The factor $(n^2+2)^2/9n$ takes into account that the neodymium ions are not in a vacuum, but in a dielectric medium (n is the refractive of the solvent; i.e. $n=1.4101$ for 1-pentanol). Finally, the $\langle J\|U^{(\lambda)}\|J'\rangle$ are reduced matrix elements. The Ω_λ parameters can be determined by a standard-least squares fitting method.

The intensity calculations for neodymium(III) hexanoate in 1-pentanol are given in Table 3. The Judd–Ofelt theory is able to give an adequate description of the intensities of the f–f transitions in the trivalent neodymium ion. For the other neodymium(III) soaps, the calculations are analogous. The intensity parameters for the neodymium(III) soaps are listed in Table 4. For all the systems, the order of the parameter values is: $\Omega_4<\Omega_2<\Omega_6$. There is no increase or decrease of the value of the Ω_4 parameter as a function of the chain length of the alkanoate group, but the values go through a maximum value for neodymium(III) hexanoate. However, the value of the Ω_2 parameter slightly increases with increasing chain length, from $(5.67\pm0.38)\cdot10^{-20}$ cm^2 for neodymium(III) butanoate to $(6.52\pm0.46)\cdot10^{-20}$ cm^2 for neodymium(III) octanoate. The greatest increase is observed between the butanoate and the pentanoate complex. For the Ω_6 parameter, an increase is observed between the butanoate and the pentanoate complex, but this parameter remains fairly constant when increasing the chain length of the alkanoate group. The trends in the parameters are visualised in Fig. 2. The parameter values are not low, but the values are not extremely high either. This can be attributed to the lack of strong polarisable groups (e.g. aromatic groups) in the ligands. Although the chain length has some influence on the spectral intensities, the optical properties are in the first place determined by the nature of the solvent. The slight increase of the Ω_2 parameter with increasing chain length can be attributed to a higher polarisability of a compound with a long alkyl chain. The trends of the Ω_4 and Ω_6 parameters are more difficult to rationalise.

Table 2
Experimental and calculated free-ion levels of Nd(III) hexanoate in 1-pentanol[a]

Level	E_{exp} (cm^{-1})	E_{calc} (cm^{-1})
$^4I_{9/2}$	–	103
$^4I_{11/2}$	–	1929
$^4I_{13/2}$	–	3877
$^4I_{15/2}$	–	5906
$^4F_{3/2}$	11 514	11 514
$^4F_{5/2}$	12 485	12 521
$(^2H,^4F)_{9/2}$	–	12 603
$^4F_{7/2}$	13 415	13 467
$^4S_{3/2}$	13 608	13 559
$^4F_{9/2}$	14 703	14 707
$^2H(2)_{11/2}$	15 908	15 874
$^4G_{5/2}$	17 195	17 239
$(^4G,^2G(1))_{7/2}$	–	17 274
$^4G_{7/2}$	19 042	19 068
$^2K_{13/2}$	–	19 440
$^4G_{9/2}$	–	19 465
$(^2G(1),^2G(2))_{9/2}$	21 026	21 020
$(^2D(1),^2P)_{3/2}$	21 259	21 295
$^2K_{15/2}$	–	21 392
$^4G_{11/2}$	–	21 444
$^2P_{1/2}$	23 334	23 321
$^2D(1)_{5/2}$	23 818	23 826
$(^2P,^2D(1))_{3/2}$	26 209	26 225
$^4D_{3/2}$	28 086	28 180
$^4D_{5/2}$	28 422	28 342
$^4D_{1/2}$	28 735	28 709
$^2I_{11/2}$	29 291	29 287
$^2L_{15/2}$	–	30 001
$^4D_{7/2}$	30 352	30 409
$^2I_{13/2}$	–	30 622
$^2L_{17/2}$	–	31 449
$^2H(1)_{9/2}$	–	32 802
$^2D(2)_{3/2}$	33 391	33 373
$^2H(1)_{11/2}$	–	34 139
$(^2D(2),^4D)_{5/2}$	34 276	34 259
$(^2F(2),^2F(1))_{5/2}$	38 426	38 361
$(^2F(2),^2F(1))_{7/2}$	39 663	39 729
$(^2G(2),^2G(1))_{9/2}$	–	47 562
$(^2G(2),^2G(1))_{9/2}$	–	48 532
$^2F(1)_{7/2}$	–	66 034
$(^2F(1),^2F(2))_{5/2}$	–	67 236

[a] The free-ion parameters used for the calculation can be found in Table 1.

From a study of the spectroscopic properties, it is difficult to determine the first coordination sphere around the neodymium(III) ion. In the solid state, these type of compounds form a double layer structure [24,25], but it can be expected that this layer structure is lost after dissolution in the solvent. The only fact we can sure about is that in solution, the lanthanide carboxylate ratio is 1:3. Besides the carboxylate groups, pentanol molecules will be present in the first coordination sphere, so that the coordination number of the neodymium(III) ion is 8 or 9. The number of pentanol molecules will depend on the coordination mode of the carboxylate ions (monodentate or bidentate). The possibility of an equilibrium between carboxylate groups with a monodentate and a bidentate coordination cannot be excluded. The small variation of the Ω_λ parameters with increasing chain length and the similarity of the band shapes of the transitions in the absorption spectrum indicate that the coordination of the neodymium(III) ion changes little or not with the lengths of the alkyl chain of the fatty acid.

4. Conclusions

The spectroscopic properties of the neodymium(III) soaps in 1-pentanol were investigated. The intensities of the f–f transitions of Nd(III) were parameterised within the framework of the Judd–Ofelt theory. Although some influence of the chain length on the Ω_λ intensity parameters is observed, this influence is small. The values of the Ω_4 parameter go through a maximum for neodymium(III) hexanoate. An increase of the parameter values with increasing chain lengths is observed for the Ω_2 and the Ω_6 parameters. The transitions are not very intense in comparison to systems with highly polarisable ligands (i.e. ligands containing phenyl groups). For all the neodymium(III) soaps, the order of the parameters is $\Omega_4 < \Omega_2 < \Omega_6$.

Table 3
Experimental and calculated dipole strengths for the transitions in the absorption spectrum of neodymium(III) hexanoate in 1-pentanol[a]

Transition $\leftarrow ^4I_{9/2}$	$\bar{\nu}$ (cm^{-1})	D_{exp} (10^{-6} Debye^2)	D_{calc} (10^{-6} Debye^2)	$D_{exp} - D_{calc}$ (10^{-6} Debye^2)	D_{calc}/D_{exp}
$^4F_{3/2}$	11 510	382	426	−44	1.12
$^2H_{9/2},^4F_{5/2}$	12 490	1549	1502	+47	0.97
$^4F_{7/2},^4S_{3/2}$	13 340	1501	1566	−65	1.04
$^4F_{9/2}$	14 700	104	110	−6	1.06
$^2H_{11/2}$	15 910	25	27	−2	1.08
$^4G_{5/2},^2G_{7/2}$	17 200	2633	2647	−14	1.01
$^4G_{7/2},^2K_{13/2},^4G_{9/2}$	19 250	898	715	+183	0.80
$^2K_{15/2},^4G_{11/2},^2D_{3/2},^2G_{9/2}$	21 390	206	149	+57	0.72
$^2P_{1/2}$	23 330	20	50	−30	1.67
$^2I_{11/2},^4D_{1/2},^4D_{3/2},^4D_{5/2}$	28 320	733	798	−65	1.09

[a] The Judd–Ofelt parameters used for the intensity calculation are: $\Omega_2 = (6.24 \pm 0.42) \cdot 10^{-20}$ cm^2, $\Omega_4 = (4.48 \pm 0.49) \cdot 10^{-20}$ cm^2 and $\Omega_6 = (7.90 \pm 0.37) \cdot 10^{-20}$ cm^2. The R.M.S. value is $85 \cdot 10^{-6}$ Debye^2. All the transitions start from the $^4I_{9/2}$ ground state.

Table 4
Judd–Ofelt intensity parameters for neodymium(III) soaps in 1-pentanol

Compound	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 (10^{-20} cm^2)
Neodymium(III) butanoate	5.67±0.38	3.75±0.44	6.93±0.34
Neodymium(III) pentanoate	6.20±0.41	4.34±0.48	7.76±0.37
Neodymium(III) hexanoate	6.24±0.42	4.48±0.49	7.90±0.37
Neodymium(III) heptanoate	6.43±0.52	4.22±0.61	7.86±0.46
Neodymium(III) octanoate	6.52±0.46	3.96±0.54	8.06±0.41

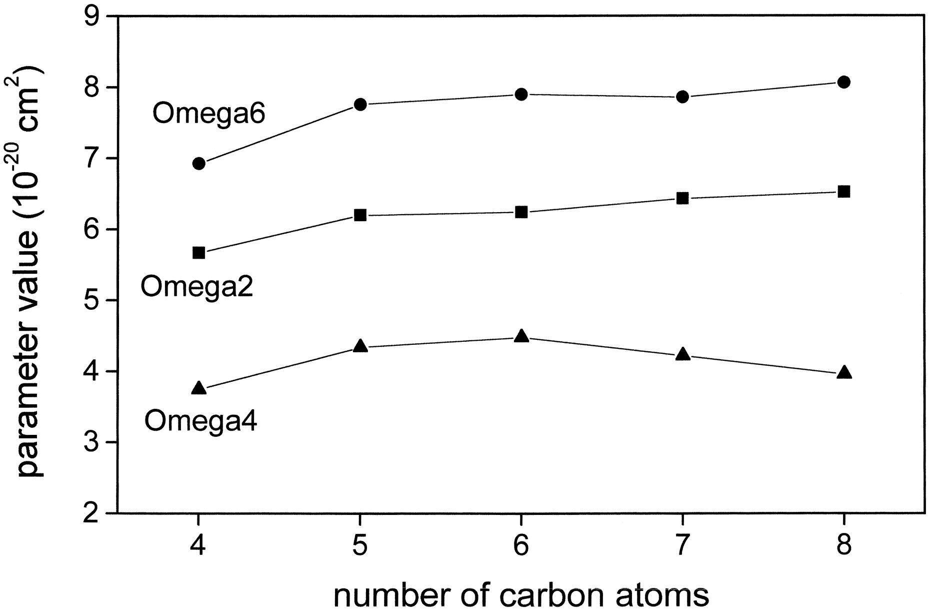

Fig. 2. Dependence of the values of the Ω_λ intensity parameters of neodymium(III) soaps in 1-pentanol on the chain length of the alkanoate group.

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