

Spectroscopic Properties of Nd³⁺ Complexes with 2,2'-Dipyridine and 1,10-Phenanthroline

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(Received December 2, 1986)

Abstract

Absorption spectroscopy studies of the hydrated and anhydrous Nd³⁺ perchlorates in CH₃OH with different concentrations of N-donor ligands 2,2'-dipyridine (Dipy) and 1,10-phenanthroline (Phe) are presented in this paper. Solid complexes of neodymium perchlorate with Dipy and Phe were also isolated.

Analysis of the intensities of f–f transitions expressed in terms of oscillator strengths and Judd–Ofelt parameters τ_λ indicate that the electron spectroscopy method can be successfully applied to the investigation of Ln³⁺ ion coordination processes in nonaqueous solvents with N-donor ligands.

It was proved that Dipy is a significantly weaker ligand than Phe for Nd³⁺ ion. Most stable species of Nd³⁺–Phe complexes which exist in solution are species with 2 and 4 Phe molecules.

Introduction

In our recent papers [1, 2] we investigated systematically spectral properties of the lanthanide polyaminoacid complexes (with NTA and EDTA) where a very weak Ln–N bond exists. Looking for a stronger Ln–N interaction, in the present paper, we have investigated spectral properties of the Nd³⁺–Dipy and Nd³⁺–Phe complexes, particularly the influence of the stronger Ln–N bond on the spectral intensities of f–f transitions in solution and in the solid phase.

IR spectral measurements provide evidence that in these complexes N-donor ligands are coordinated in the first coordination sphere of the lanthanide ion [3–6]. It has been stated that for mixed chloride–N-donor lanthanide complexes 2,2'-Dipy is a stronger ligand for the heavy lanthanide ions, whereas 1,10-Phe is stronger for the lighter ones [4]. Not many

crystal structure data are available for these complexes. A mixed La(NO₃)₃(Dipy)₂ crystal was investigated by Karaghoully and Wood [7] and Tb(Dipy)₂(NO₃)₃ by Sinha and Moss [8].

The coordination polyhedron has coordination number 10 and average bond distances are 2.66 and 2.60 Å for La–N and La–O; 2.50 and 2.47 Å for Tb–N and Tb–O respectively. The La–N bond distance is distinctly shorter than the bond distance in the EDTA lanthanum complex [9], rather close to that of the Pr(NTA)₂·H₂O crystal with coordination number 9 [10].

Electronic spectroscopy data for these complexes both in solution and in the solid phase are far from being complete. Sinha [11] measured spectra of NdCl₃ and NdCl₃·6H₂O with Dipy and Phe in alcohol and water solvents. The author found some nephelauxetic effects [12] in reflection spectra of mixed Nd³⁺–chloride dipyridine complexes in the solid phase and calculated τ_λ parameters for solutions. However, it is rather difficult to obtain precise information, both about the fitting procedure of these parameters and the role played by the Cl ion and molecules of ligand and solvent present in the first coordination sphere of lanthanide ion as well as their influence on the nephelauxetic effect.

With both Dipy and Phe ligands lanthanide ions form mixed complexes only. In order to consider the influence of 2,2'-Dipy and 1,10-Phe ligands it is necessary to analyse the role which is played by other ligands (anions and/or solvent molecules) in the mixed first coordination sphere of lanthanide ions. The spectral properties of solution spectra of Nd(ClO₄)₃ in alcoholic solvents are relatively well known [13], so we decided to use CH₃OH as solvent for the investigation of the solution spectra of Nd³⁺–Dipy and Phe complexes.

Experimental

Nd(ClO₄)₃ was prepared from Nd₂O₃ 99.9% (Koch-Light) by the method given by Forsberg and Moeller [14]. Anhydrous Nd(ClO₄)₃ was prepared by

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slow heating of hydrated neodymium perchlorate under vacuum (1 mm Hg) for at least 120 h as suggested by Thomson [15]. All the salts used were fully analysed; 1,10-phenanthroline was dehydrated under vacuum (1 mm Hg) for at least one week. All anhydrous reagents were checked for water contamination by the IR method. Such samples, where no O–H stretching bands were observed, were used for the spectral measurements. Alcohols used as solvents of anhydrous salts were dried using molecular sieves (A-4). Nd(Dipy)₃(ClO₄)₃·xH₂O was crystallized from a 100% methanol solution of hydrated neodymium perchlorate with excess of the Dipy ligand; the same method was applied for preparation of Nd³⁺ complex with Phe. The resulting complex contains 4 phenanthroline molecules – Nd(Phe)₄(ClO₄)₃. All complexes were fully analysed.

Measurements and Calculations

Spectral measurements were made on the Cary 14 spectrophotometer at 293 K, at the available spectral range (11 000–30 000 cm⁻¹). UV bands of the Nd³⁺ ion f–f transitions have not been used for the intensity calculations, because the basic lines of the absorption bands were not well determined due to the strong absorption of ligands in this spectral region.

Reflection spectra were measured on the Beckman UV 5240 spectrophotometer with a reflectance attachment. The samples of complexes were diluted by MgO which was also used as a standard. Experimental oscillator strength values of solution absorption bands were obtained by the graphical integration of the area under the absorption curves after appropriate correction of the base line. τ_λ parameter values were calculated from the experimental oscillator strength values applying the Judd–Ofelt equation in the modified form:

$$P = \sum_{\lambda=2, 4, 6} \tau_\lambda \sigma (f^N_{\psi_J} \| U^{(\lambda)} \| f^N_{\psi'_J})^2 / (2J + 1)$$

TABLE Ia. The Oscillator Strength Values ($P \times 10^6$) of f–f Transitions for Hydrated and Anhydrous Neodymium Perchlorates with Dipy in CH₃OH

Nd:Dipy	Nd(ClO ₄) ₃ ·6H ₂ O ($c_{\text{Nd}^{3+}} = 1.26 \times 10^{-2}$ M)				Nd(ClO ₄) ₃ ($c_{\text{Nd}^{3+}} = 2.50 \times 10^{-2}$ M)			
	1:0	1:2	1:4	1:8	1:0	1:2	1:4	1:8
Terms								
² D _{5/2} , ² P _{1/2}	0.41	0.40	0.38	0.39	0.38	0.40	0.40	0.39
⁴ G _{11/2} , (² D, ² F) _{3/2} , ² G _{9/2} , ² K _{15/2}	1.87	2.01	1.92	1.97	1.70	1.77	1.74	1.77
⁴ G _{9/2} , ² K _{13/2} , ⁴ G _{7/2}	6.33	6.43	6.67	6.88	6.38	6.45	6.33	6.58
⁴ G _{5/2} , ² G _{7/2}	12.02	12.65	13.07	13.60	11.96	12.84	13.08	13.82
⁴ F _{9/2}	0.59	0.65	0.61	0.61	0.63	0.60	0.61	0.60
² S _{3/2} , ⁴ F _{7/2}	8.38	8.42	8.47	8.61	8.31	8.40	8.45	8.55
⁴ F _{5/2} , ² H _{9/2}	9.09	8.56	8.67	8.65	8.42	8.57	8.50	8.47
⁴ F _{3/2}	2.41	2.39	2.31	2.35	2.44	2.37	2.47	2.32

where σ is the wave number (in cm⁻¹), $U^{(\lambda)}$ are the matrix elements of the unit tensor operator calculated by Carnall *et al.* [16], $f^N_{\psi_J}$, $f^N_{\psi'_J}$ are the initial and final states of the particular electronic transition respectively, and J is the total quantum number.

For the best assignments of particular electronic levels, the calculations were performed for the different sets of levels and the results with minimal mean square errors were considered:

$$S = \left(\frac{\sum (\Delta P)^2}{i - 3} \right)^{1/2}$$

where i is the number of available equations and ΔP is the difference between experimental oscillator strength value and calculated oscillator strength value for fitted τ_λ parameters. The absorption spectra of Nd³⁺–Dipy and Nd³⁺–Phe complexes in CH₃OH were measured for different M:L ratios (from 1:0.5–1:8).

Results and Discussion

The results of the Nd³⁺–Dipy system spectral measurements in methanol solutions for hydrated and anhydrous neodymium perchlorates are collected in Table I. For these systems only a small increase of f–f ‘hypersensitive’ transition intensity is observed in comparison with the spectra of Nd(ClO₄)₃ in pure methanol solvent. Slightly higher intensities are observed for anhydrous species.

The results of corresponding measurements of the Nd³⁺–perchlorates with Phe are given in Tables II and III. In these systems, the distinct increase of f–f transition intensities is observed, both in comparison with the spectra of Nd(ClO₄)₃ in pure methanol solvent and with the Nd³⁺–Dipy system respectively. Similarly a slight increase of intensities is observed for anhydrous species. The most differences are

TABLE Ib. Judd–Ofelt Parameter Values (τ_λ) for Hydrated and Anhydrous Neodymium Perchlorates with Dipy in CH₃OH

Nd:Dipy	Nd(ClO ₄) ₃ ·6H ₂ O ($c_{\text{Nd}^{3+}} = 1.26 \times 10^{-2}$ M)				Nd(ClO ₄) ₃ ($c_{\text{Nd}^{3+}} = 2.50 \times 10^{-2}$ M)			
	1:0	1:2	1:4	1:8	1:0	1:2	1:4	1:8
a								
$\tau_2 \times 10^9$	1.05 ± 0.33	1.70 ± 0.40	1.78 ± 0.53	2.07 ± 0.78	1.15 ± 0.36	1.79 ± 0.52	1.79 ± 0.45	2.69 ± 0.62
$\tau_4 \times 10^9$	8.97 ± 0.95	8.83 ± 0.96	9.00 ± 0.90	8.92 ± 0.98	8.76 ± 0.68	8.60 ± 0.79	8.69 ± 0.69	8.89 ± 0.90
$\tau_6 \times 10^9$	9.22 ± 0.46	9.20 ± 0.51	9.15 ± 0.61	9.30 ± 0.57	9.08 ± 0.43	9.07 ± 0.38	8.99 ± 0.33	9.11 ± 0.45
$S \times 10^7$	4.28	4.77	5.64	5.28	4.08	3.56	3.07	4.21
b								
$\tau_2 \times 10^9$	0.97 ± 0.36	1.63 ± 0.41	1.58 ± 0.58	2.00 ± 0.80				
$\tau_4 \times 10^9$	9.05 ± 0.96	8.63 ± 0.88	9.09 ± 0.84	8.94 ± 0.93				
$\tau_6 \times 10^9$	9.18 ± 0.46	9.14 ± 0.52	9.10 ± 0.64	9.30 ± 0.58				
$S \times 10^7$	4.30	4.75	5.89	5.39				

^a2D_{5/2}, 2P_{1/2} states are included.

^b2D_{5/2}, 2P_{1/2} states are omitted.

observed, as usual [17], for both oscillator strength values of the ‘hypersensitive’ transition and τ_2 parameter values. Some authors have suggested a different spectral mechanism for the ‘hypersensitive’ transition ${}^4G_{5/2}$, ${}^2G_{7/2} \leftarrow {}^4I_{9/2}$ than for other f–f transitions.

The role of this transition is important in the evaluation of τ_2 parameters (largest matrix element U^2 value), even if the τ_2 parameter value in the case of the Nd³⁺ ion is evaluated from 6 f–f transitions. Unfortunately, the error in evaluation of this parameter value is too large for an unequivocal statement that the relation between the value of oscillator strength of ‘hypersensitive’ transition (P_{hyp}) and τ_2 parameter values *versus* ligand concentration has the same character.

A general feature of the intensity changes enables us, however, to conclude that intensity changes are related to the complexation process of the N-donor ligand, which exchanges the solvent molecules in the first coordination sphere of the lanthanide ion. This process is clearly seen in Fig. 1, where both P_{hyp} and τ_2 parameter values are presented as a function of the total ligand concentration. These results clearly indicate that Dipy is significantly a weaker bonding ligand for Nd³⁺ ion than Phe. It has to be pointed out, that in our research, entirely corresponding systems were considered.

A more detailed inspection of the data confirmed this conclusion very well. It is particularly visible in Fig. 2, where distinct changes in the shape, energy and intensity of the ‘hypersensitive’ transition is observed for the Nd³⁺–Phe system, whereas for Nd³⁺–Dipy only a slight increase in intensity can be noted. A smaller, but significant, influence of the ligand concentration is observed also for other f–f transitions (Fig. 3). There is good agreement with the evaluated values of τ_4 and τ_6 parameters, which are,

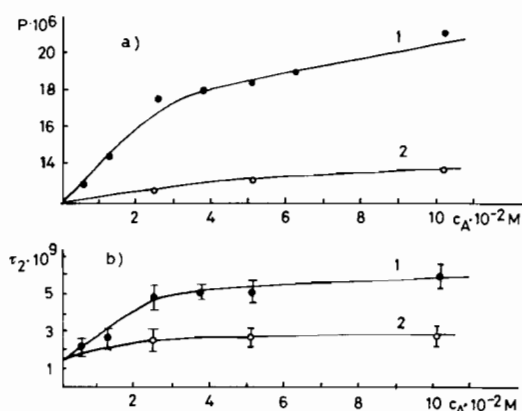


Fig. 1. Oscillator strength of ‘hypersensitive’ transition ${}^4G_{5/2}$, ${}^2G_{7/2} \leftarrow {}^4I_{9/2}$ (a) and τ_2 parameter value (b) of hydrated neodymium perchlorate as a function of the Phe and Dipy concentration. 1: Nd³⁺–Phe —●—; 2: Nd³⁺–Dipy —○—; $c_{\text{Nd}^{3+}} = 1.26 \times 10^{-2}$ M, $d = 5$ cm.

besides τ_2 , also higher for the Nd³⁺–Phe system than for the pure alcohol solvates (see Tables II and III).

Above a M:L ratio of 1:2 the changes of all τ_2 parameter values are distinctly smaller which suggest a particular stability of the Nd(Phe)₂(solv)_y species in solution. Again more distinct changes are seen for the system with a high ligand excess, which can be related rather to the formation of Nd(Phe)₄(solv)_{y-2} species (see Table III). This is confirmed by the fact that in this form the Phe complex of Nd³⁺ is isolated in the solid phase. Even reflection spectra of polycrystalline samples are very similar to the solution spectra with a M:L ratio higher than 1:4 (Fig. 4). It should be noted as well that synthesis of the Nd³⁺–Dipy complexes in the solid phase is very difficult, and only species with 3 Dipy molecules can be isolated in a poor crystalline form.

TABLE II. The Oscillator Strength Values ($P \times 10^6$) of $f-f$ Transitions and Judd–Ofelt Parameter Values (τ_λ) of Hydrated Neodymium Perchlorate with Phe in Methanol ($c_{Nd^{3+}} = 1.26 \times 10^{-2} M$)

Nd:Phe	1:0	1:0.5	1:1	1:2	1:3	1:4	1:5	1:8
Terms								
$^2D_{5/2}, ^2P_{1/2}$	0.41	0.43	0.42	0.46	0.44	0.39	0.40	0.40
$^4G_{11/2}, (^2D, ^2F)_{3/2}, ^2G_{9/2}, ^2K_{15/2}$	1.86	1.80	1.77	2.07	2.16	2.21	2.15	2.29
$^4G_{9/2}, ^2K_{13/2}, ^4G_{7/2}$	6.33	7.56	7.73	7.72	8.24	8.57	8.75	8.56
$^4G_{5/2}, ^4G_{7/2}$	12.02	12.83	14.53	17.98	18.24	18.87	19.49	21.62
$^4F_{9/2}$	0.59	0.60	0.62	0.67	0.63	0.65	0.63	0.67
$^2S_{3/2}, ^4F_{7/2}$	8.38	9.00	9.23	9.40	9.98	9.99	10.00	9.98
$^4F_{5/2}, ^2H_{9/2}$	9.08	9.12	9.50	9.88	9.96	9.96	9.95	9.97
$^4F_{3/2}$	2.41	2.40	2.44	2.25	2.54	2.49	2.51	2.41
$\tau_2 \times 10^9$	1.05 ± 0.33	1.18 ± 0.48	1.83 ± 0.55	4.04 ± 0.80	4.06 ± 0.80	4.23 ± 0.72	4.51 ± 0.78	5.43 ± 0.82
$\tau_4 \times 10^9$	8.97 ± 0.96	9.47 ± 1.03	10.11 ± 0.98	9.97 ± 1.08	10.26 ± 1.00	10.44 ± 1.02	10.55 ± 1.04	10.62 ± 1.07
$\tau_6 \times 10^9$	9.22 ± 0.46	9.61 ± 0.64	9.90 ± 0.62	10.58 ± 0.62	10.62 ± 0.61	10.52 ± 0.68	10.07 ± 0.80	10.56 ± 0.82
$S \times 10^7$	4.28	4.96	5.72	5.17	6.64	6.22	6.32	6.60

TABLE III. The Oscillator Strength Values ($P \times 10^6$) of $f-f$ Transitions and Judd–Ofelt Parameter Values (τ_λ) of Anhydrous Neodymium Perchlorate with Phe in Methanol ($c_{Nd^{3+}} = 1.44 \times 10^{-2} M$)

Nd:Phe	1:0	1:1	1:2	1:3	1:4	1:5	1:8
Terms							
$^2D_{5/2}, ^2P_{1/2}$	0.42	0.39	0.41	0.39	0.40	0.40	0.44
$^4G_{11/2}, (^2D, ^2F)_{3/2}, ^2G_{9/2}, ^2K_{15/2}$	1.84	1.96	1.99	2.09	1.99	2.18	2.20
$^4G_{9/2}, ^2K_{13/2}, ^4G_{7/2}$	7.66	7.88	7.99	8.05	9.04	9.20	9.44
$^4G_{5/2}, ^4G_{7/2}$	12.14	15.02	17.43	18.47	21.19	21.47	22.56
$^4F_{9/2}$	0.71	0.71	0.73	0.69	0.72	0.73	0.72
$^2S_{3/2}, ^4F_{7/2}$	7.65	8.84	8.89	9.19	9.63	9.65	9.87
$^4F_{5/2}, ^2H_{9/2}$	8.74	8.83	9.02	9.20	9.52	9.58	9.86
$^4F_{3/2}$	2.26	2.26	2.43	2.53	2.60	2.58	2.57
$\tau_2 \times 10^9$	1.12 ± 0.48	2.20 ± 0.75	3.78 ± 0.63	3.98 ± 0.62	5.05 ± 0.82	5.07 ± 0.86	5.56 ± 0.83
$\tau_4 \times 10^9$	9.46 ± 0.93	10.09 ± 0.96	10.20 ± 0.91	10.38 ± 0.98	11.50 ± 0.98	11.70 ± 0.96	11.75 ± 0.86
$\tau_6 \times 10^9$	9.25 ± 0.48	9.31 ± 0.77	9.47 ± 0.68	9.66 ± 0.62	9.93 ± 0.80	10.00 ± 0.84	10.49 ± 0.91
$S \times 10^7$	6.22	7.31	6.33	5.74	7.33	7.33	7.64

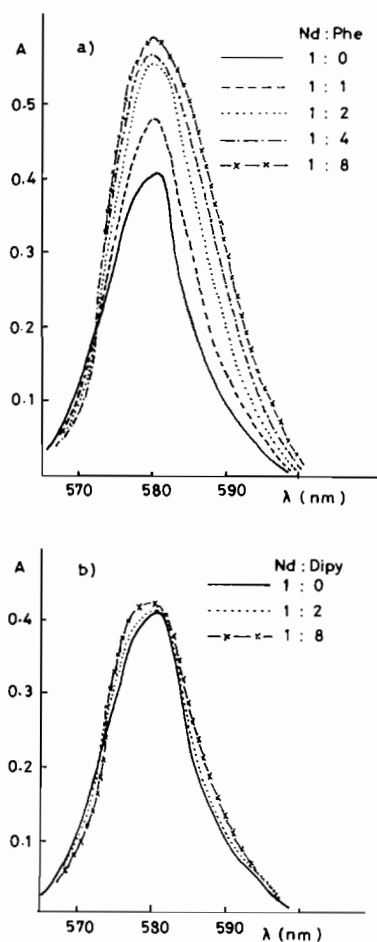


Fig. 2. The effect of (a) Phe and (b) Dipy concentration on the 'hypersensitive' transition ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$ in the absorption spectrum of the hydrated neodymium perchlorate, $c_{Nd^{3+}} = 1.26 \times 10^{-2}$ M, $d = 5$ cm.

Electron spectroscopy appears quite a sensitive method for investigating the coordination process in solution even for lanthanide complexes with N-donor ligands in nonaqueous solvents. However for a more detailed consideration of these effects the examination of mixed Ln-N-donor complexes with other solvents and with other anions which can be present in solution in the first coordination sphere of the lanthanide cation will be necessary. These results will be the subject of further papers. We hope as well that, in correlation with the luminescence spectroscopy data, these results will be helpful in explaining possible mechanisms in f-f spectral transitions.

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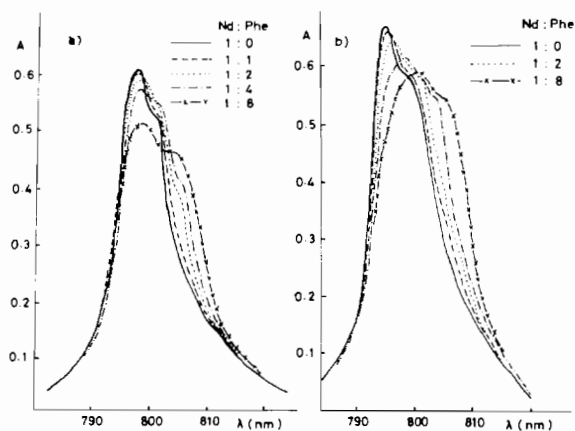


Fig. 3. The effect of the Phe concentration on the ${}^4F_{5/2}, {}^2H_{9/2} \leftarrow {}^4I_{9/2}$ transition in the absorption spectrum of: (a) $Nd(ClO_4)_3$ hydrated, $c_{Nd^{3+}} = 1.26 \times 10^{-2}$ M, $d = 5$ cm; (b) $Nd(ClO_4)_3$ anhydrous, $c_{Nd^{3+}} = 1.44 \times 10^{-2}$ M, $d = 5$ cm.

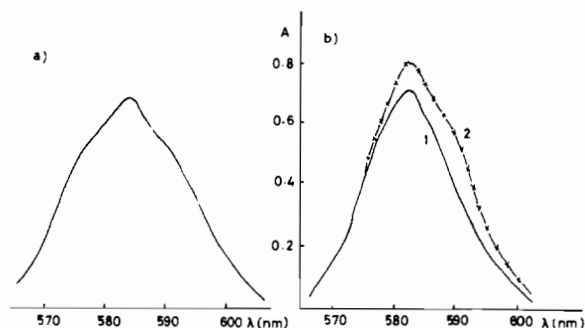


Fig. 4. (a) The ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$ transition in the reflectance spectrum of the solid $[Nd(Phe)_4(solv)_y]$ (intensities in arbitrary units). (b) The ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$ transition in the absorption spectrum of the anhydrous neodymium perchlorate with Phe in CH_3OH solutions. (1) $c_{Nd^{3+}}:c_{Phe} = 1:4$; (2) $c_{Nd^{3+}}:c_{Phe} = 1:8$; $c_{Nd^{3+}} = 1.44 \times 10^{-2}$ M, $d = 5$ cm.

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