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# Neodimium(III) Luminescence in the Mixed Ligand Compounds with β-Diketones

**I. V. Kalinovskaya, A. Yu. Mamaev, and V. E. Karasev**

*Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences,*
*pr. 100-letiya Vladivostoka 159, Vladivostok, 690022 Russia*
*e-mail: kalinovskaya@ich.dvo.ru*

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**Abstract**—The luminescent spectral characteristics of neodymium(III) tris- and tetrakis-β-diketonates and β-diketonate acido complexes were investigated. The dependence between the intensity of the luminescence and the composition of the coordination sphere of the complexes was revealed. The most intense luminescence in the IR region possess the neodymium(III) compounds which are the mixed ligand complexes with β-diketones and phosphorus-containing neutral ligands.

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The neodymium(III) compounds can be used as converters of ultraviolet radiation into the near-infrared radiation, which is important for biomedical problems [1]. These converters can be used to increase the sensitivity in the UV region of silicon detectors whose spectral sensitivity peak falls to the near infrared region, and also applied as fluorescent labels in immunofluorescence analysis [2]. The results have been published on the study of the neodymium ions IR luminescence in the homo- and heterobinuclear complexes based on *p*-*tert*-butylcalix[3]arene, in the complexes with β-diketones [3], and porphyrins [4]. As β-diketones the long-chain derivatives of acetylacetone were used containing the residues of perfluoroenantic and perfluoropelargonic acids in the fluorinated moiety [4]. The luminescence properties of solutions of these luminescent compounds were mainly studied [2–4, 5].

The purpose of this study is revealing the spectral-luminescent properties of mixed-ligand acido complexes of neodymium(III) of the composition $Nd(NO_3)_3 \cdot 2D$, where D is 1,10-phenanthroline (Phen), triphenylphosphine oxide (**I**), dihexylsulfoxide (**II**); the neodymium tetrakis-β-diketonates of the composition $M[Nd(\beta\text{-dik})_4]$, where M is Rb or K, β-dik is dibenzoylmethane, (**III**), thenoyltrifluoroacetone (**IV**), hexafluoroacetylacetone (**V**); tris-β-diketonates of the composition $Nd(\beta\text{-dik})_3 \cdot 2D$, where β-dik means β-diketones: dibenzoylmethane (**III**), thenoyltrifluoroacetone (**IV**), hexafluoroacetylacetone (**V**), heptafluorodimethyloctadione (fod); D comprises 1,10-phenanthroline (Phen), triphenylphosphine oxide (**I**), and hexamethylphosphoramide (**VI**).

The excitation energy of the triplet ($T_1$) levels of β-diketones falls to the range of 19600–23000 $cm^{-1}$, which provides a ~7500 $cm^{-1}$ gap between the ligand triplet level and the Nd excited level. In the case of ytterbium(III) ions this gap is much larger and amounts to ~10000–13000 $cm^{-1}$ [3]. Nonradiative energy losses in the case of the neodymium complex compounds can be substantially smaller than in the ytterbium compounds. In this connection, we have synthesized a series of the neodymium acido complexes and β-diketonates of tris and tetrakis type, and studied their fluorescence properties.

Study of the synthesized neodymium compounds using powder X-ray diffraction method confirmed their individuality (Table 1). Phase analysis indicated the absence of lines of source materials and potential contaminants. The obtained complexes are stable in air.

The highly efficient energy transfer from the organic moiety of the complex (β-diketone, a neutral ligand) to the neodymium ion is largely determined by the ligand absorption and the efficiency of the transfer from the ligand to the neodymium ion. Therefore we have studied the absorption spectra of the neodymium mixed ligand complexes with β-diketones, nitrogen-

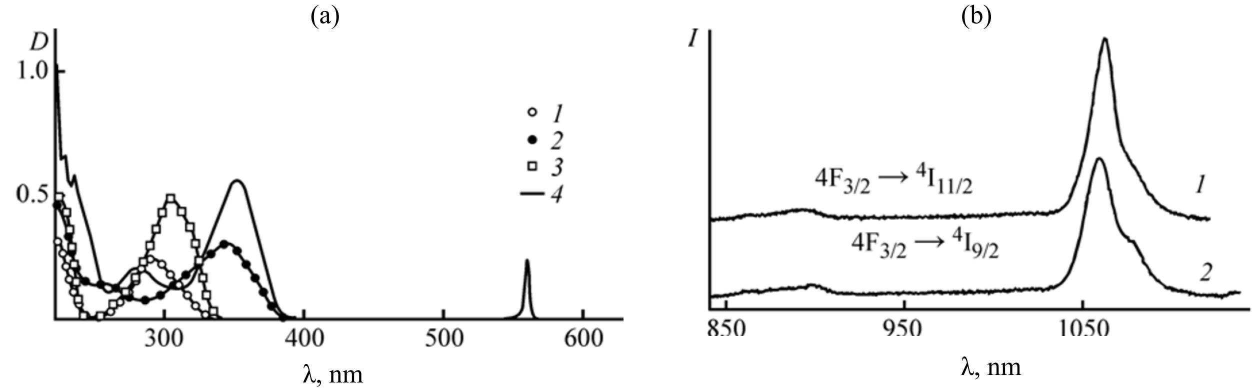

**Fig. 1.** (a) (*1*) Absorption spectra of $Nd(C_5O_2F_6H)_3{\cdot}2(C_6H_5)_3PO$, (*2*) $Nd(C_{10}O_2F_7H_{10})_3{\cdot}2$**I**, (*3*) $Nd(C_6H_4O_2F_3S)_3{\cdot}2\ (C_6H_5)_3PO$, and (*4*) $Nd(C_{15}H_{12}O_2)_3{\cdot}2(C_6H_5)_3PO$. (b) Luminescence spectra of (*1*) $Nd(C_5O_2F_6H)_3{\cdot}2(C_6H_5)_3PO$ and (*2*) $Nd(C_5O_2F_6H)_3{\cdot}2(C_6H_5)_3PO$.

and phosphorus-containing neutral ligands (see Fig. 1a). As seen from the figure, the obtained neodymium complexes absorb in the wavelength range 220–380 nm. In the absorption spectra, to the absorption bands of β-diketones are added the bands corresponding to π–π* transitions of the neutral molecules forming the adducts: Phen, **I**, **IV**, and **VI**.

**Table 1.** X-ray diffraction data of neodymium compounds with β-diketones and nitrogen- and phosphorus-containing neutral ligands

| Nd(**V**)$_3$·2**I** | | Eu(**V**)$_3$·2**I** | | Nd(**V**)$_3$·2**VI** | |
|---|---|---|---|---|---|
| *d*, Å | *I*/*I*$_0$ | *d*, Å | *I*/*I*$_0$ | *d*, Å | *I*/*I*$_0$ |
| 15.60 | 10.0 | 15.61 | 10.0 | 10.28 | 100.0 |
| 12.57 | 9.2 | 12.50 | 9.2 | 9.18 | 95.62 |
| 10.2 | 100.0 | 10.2 | 100.0 | 8.87 | 85.60 |
| 9.59 | 30.4 | 9.57 | 30.8 | 7.69 | 10.50 |
| 9.16 | 5.0 | 9.19 | 6.1 | 7.14 | 30.00 |
| 6.69 | 10.0 | 6.68 | 11.0 | 6.20 | 20.11 |
| 5.99 | 10.0 | 5.95 | 9.5 | 6.00 | 10.60 |
| 4.80 | 9.1 | 4.82 | 9.2 | 5.60 | 10.60 |
| 4.53 | 42.5 | 4.56 | 42.0 | 5.23 | 40.00 |
| 4.34 | 15.0 | 4.33 | 15.3 | 5.00 | 40.00 |
| 4.17 | 20.9 | 4.19 | 20.9 | 4.70 | 10.00 |
| 3.70 | 15.9 | 3.69 | 16.1 | 4.54 | 20.00 |
| | | | | 4.13 | 25.00 |
| | | | | 4.15 | 10.00 |
| | | | | 3.95 | 45.0 |

Note that as in the case of β-diketones, the position and shape of the absorption bands of neutral molecules remains practically unchanged at the complexation: Only a small red shift of the bands (5–6 nm) occurs. The comparison of the absorption spectra of the mixed ligand β-diketonates shows that compounds with dibenzoylmethane and thenoyltrifluoroacetone partially absorb more long-wave radiation (λ = 360–380 nm) compared with the neodymium hexafluoroacetylacetonate and hexafluorodimethyloctadionates ob-tained by us. In addition, at increase in the concentration of the complex compounds in the solutions, in the absorption spectra appear narrow bands in the region of 576–578 nm characteristic of the neodymium(III) ion.

Figure 1b shows the fluorescence spectra of crystalline neodymium mixed ligand β-diketonates with nitrogen- and phosphorus-containing neutral ligands. Luminescence of the complex compounds in the crystalline state were measured at room temperature. The 4*f*-luminescence of neodymium ions in the synthesized compounds is observed in the region 850–1100 nm (near IR) with a maximum at 1060 nm (at the excitation in the range 500–600 nm). The fluorescence spectra of the neodymium acido complexes and β-diketonates are structured. They include two fairly strong transitions bands: the first at the $\lambda_{max}$ = 903–907 nm ($^4F_{5/2}$ – $^4I_{9/2}$), and the second at the $\lambda_{max}$ = 1060–1065 nm ($^4F_{5/2}$ – $^4I_{11/2}$). The most intense in the fluorescence spectra are the bands of $^4F_{5/2}$ – $^4I_{11/2}$ transition, consisting of 2–5 bands. We compared the intensities of the bands of $^4F_{5/2}$ – $^4I_{11/2}$ 2 transition of the synthesized neodimium complex compounds (Table 2).

**Table 2.** Relative integral intensities of the bands of $^4F_{5/2}$–$^4I_{11/2}$ transition of the neodymium(III) compounds with β-diketones and nitrogen- and phosphorus-containing neutral ligands

| Compound | $I_{rel}(^4F_{5/2}–^4I_{11/2})$, % | Compound | $I_{rel}(^4F_{5/2}–^4I_{11/2})$, % |
|---|---|---|---|
| Nd(**V**)$_3$·2**I** | 100.0 | Rb[Nd(**V**)$_4$] | 20.0 |
| Nd(**III**)$_3$·2**I** | 78.0 | K[Nd(**V**)$_4$] | 32.0 |
| Nd(**IV**)$_3$·2**I** | 93.5 | Rb[Nd(**IV**)$_4$] | 10.0 |
| Nd(fod)$_3$·2**I** | 62.5 | K[Nd(**IV**)$_4$] | 10.0 |
| Nd(**V**)$_3$·2**VI** | 58.0 | Rb[Nd(**IV**)$_4$] | 20.0 |
| Nd(**III**)$_3$·2**VI** | 56.0 | K[Nd(**IV**)$_4$] | 22.0 |
| Nd(**IV**)$_3$·2**VI** | 55.0 | R[Nd(**IV**)$_4$]·3H$_2$O | 25.0 |
| Nd(fod)$_3$·2**VI** | 52.5 | Nd(fod)$_3$·2Phen | 48.0 |
| Nd(**V**)$_3$·2Phen | 51.0 | Nd(NO$_3$)$_3$·2Phen | 8.0 |
| Nd(**III**)$_3$·2Phen | 55.0 | Nd(NO$_3$)$_3$·2**II** | 10.0 |
| Nd(**IV**)$_3$·2Phen | 65.0 | Nd(NO$_3$)$_3$·2**I** | 10.0 |

Table 2 shows that the luminescence intensity of the neodymium mixed-ligand β-diketonates with nitrogen- and phosphorus-containing neutral ligands is much higher than that of the neodymium β-diketonates of tetrakis type and the neodymium nitrates with neutral ligands. The greatest luminescence intensity show the β-diketonates with triphenylphosphine, a neutral phosphorus-containing ligand. Therewith, an increase in the length of the fluorinated moiety in going from $CF_3$ to $C_2F_7$ does not increase the luminescence intensity. We found that the relative fluorescence intensity of the neodymium β-diketonate complexes with triphenylphosphine oxide is 2.0-fold larger than that of the earlier described neodymium thenoyltrifluoroacetonate complex with 1,10-phenanthroline. The fluorescence properties of solutions of the neodymium(III) thenoyltrifluoroacetonate complex with phenanthroline were described in [4], where the luminescence intensity of this complex was compared with that of the neodymium compounds with acetylacetone phenyl derivatives having a long chain. We obtained the neodimium hexafluoroacetylacetonate isostructural with the earlier synthesized europium hexafluoroacetylacetonate with triphenylphosphine oxide. The crystal and electronic structure of the europium compound was described in detail in [5, 6]. It was found that in europium hexafluoroacetylacetonate the neutral donor triphenylphosphine oxide ligands increase the electron density on the β-diketone atoms, which leads to the stability of the β-diketonate anion and the complex compound as a whole [7].

Thus, our studies of luminescence properties of the mixed ligand neodymium(III) β-diketonates showed that among the synthesized neodimium compounds the most intense luminescence in the infrared region show the complex compounds with fluorinated β-diketones and neutral phosphorus-containing ligand triphenylphosphine oxide.

## EXPERIMENTAL

Synthesis of acido complexes and the neodymium(III) complexes with β-diketones was carried out according to the procedures in [7]. The synthesized compounds were recrystallized from ethanol. The purity of the compounds obtained was monitored by chemical elemental analysis, X-ray diffraction, UV and IR spectroscopy. The luminescence spectra were recorded on a SDL-1 spectrometer with a photomultiplier FEU-62 in the range of 1000–1100 nm. The luminescence was excited by a xenon lamp DKsSh-130 and mercury lamp DRSh-250 in the range of 500–600 nm, using the filters SZS-23 and ZhS-18. The samples were placed in Pyrex cells and examined at room temperature. The concentration of ethanol solutions of the complex compounds was $10^{-5}$ M. The absorption spectra of the obtained mixed ligand complexes were taken on a SF-256 UWI spectrophotometer.

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