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Emission and absorption properties of the eight-coordinate $[Pr(C_7H_9NO)_8](ClO_4)_3$ complex with 3,4-lutidine *N*-oxide

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Abstract

The eight-coordinate complex of praseodymium(III) with 3,4-lutidine *N*-oxide, $[Pr(C_7H_9NO)_8](ClO_4)_3$, has been synthesised and characterised by means of several spectroscopic methods. The IR and Raman spectra have been measured and are discussed. The electronic absorption, emission and excitation spectra have been recorded and are analysed in terms of possible structures. The $^3P_0 \rightarrow {}^3H_{5,6}$, $^3F_{2,4}$ emissions have been observed and selective excitation was used to assign the energy levels of Pr^{3+}. The potential application of this material as a precursor to light-conversion molecular schemes is discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Octakis Pr(III) complex; Lutidine *N*-oxide ligand; Emission and absorption properties

1. Introduction

Luminescence in rare earth (RE) compounds with organic ligands proceeds throughout intramolecular energy transfer from the excited ligand triplet states to the coordinated ion. The efficiency of this process depends on the efficiency of the organic ligand absorption, the ligand-to-lanthanide ion energy transfer and the RE luminescence. A good correlation between the excited levels of the lanthanide and the CT energy of the ligand leads to enhancement of the luminescence in such systems [1–3]. Our studies [4] suggest that the composition and structure of such compounds also play an important role. The praseodymium ion forms a very wide class of complexes with lutidine *N*-oxide derivatives. The ratio of RE to ligand in these compounds ranges from two to eight and the coordination number can be six or eight. Among them the eight-coordinate compounds of the $[PrL_8]^{3+}$ type seem to have the greatest luminescent efficiency. The crystal structures of two such compounds were determined for lanthanum and neodymium [5] which crystallize in two different monoclinic forms with $P2_1/a$ and $C2/c$ space groups, respectively. The eight-coordinate $La(PyO)_8^{3+}$ complex ion has C_2 point group symmetry and a polyhedron-like coordination of almost D_4 point group symmetry (being intermediate between a cube and a square antiprism). The $Nd(PyO)_8^{3+}$ complex ion has approximately S_8 point group symmetry with a polyhedron coordination closely resembling the square antiprism (D_{4d}). The average La–O and Nd–O distances have been determined as 2.497 and 2.407 Å, respectively [5]. In both structures, the complex cations are octahedrally surrounded by perchlorate ions, one in each structure being disordered.

As far as we know, spectroscopic studies of this complex have not yet been carried out. In the present paper the synthesis and physicochemical properties of the octakis pyridine *N*-oxide complex of praseodymium(III) are reported. The spectroscopic data are compared with those for a hexacoordinate complex of the $PrCl_3L_2(H_2O)$ type where the praseodymium/organic ligand ratio is 1:2 [4].

2. Experimental

2.1. Synthesis

A water solution of perchloric acid (4 ml) with 0.173 g praseodymium(III) oxide (99.99%) was heated at 90°C and slowly evaporated in the 95–110°C range. The obtained praseodymium perchlorate was dissolved in 10 ml 99.8% ethanol and 0.985 g 3,4-lutidine *N*-oxide was added. After 24 h storage at 4°C a yellow solid residue was obtained. The crystallized precipitate was filtered, washed three

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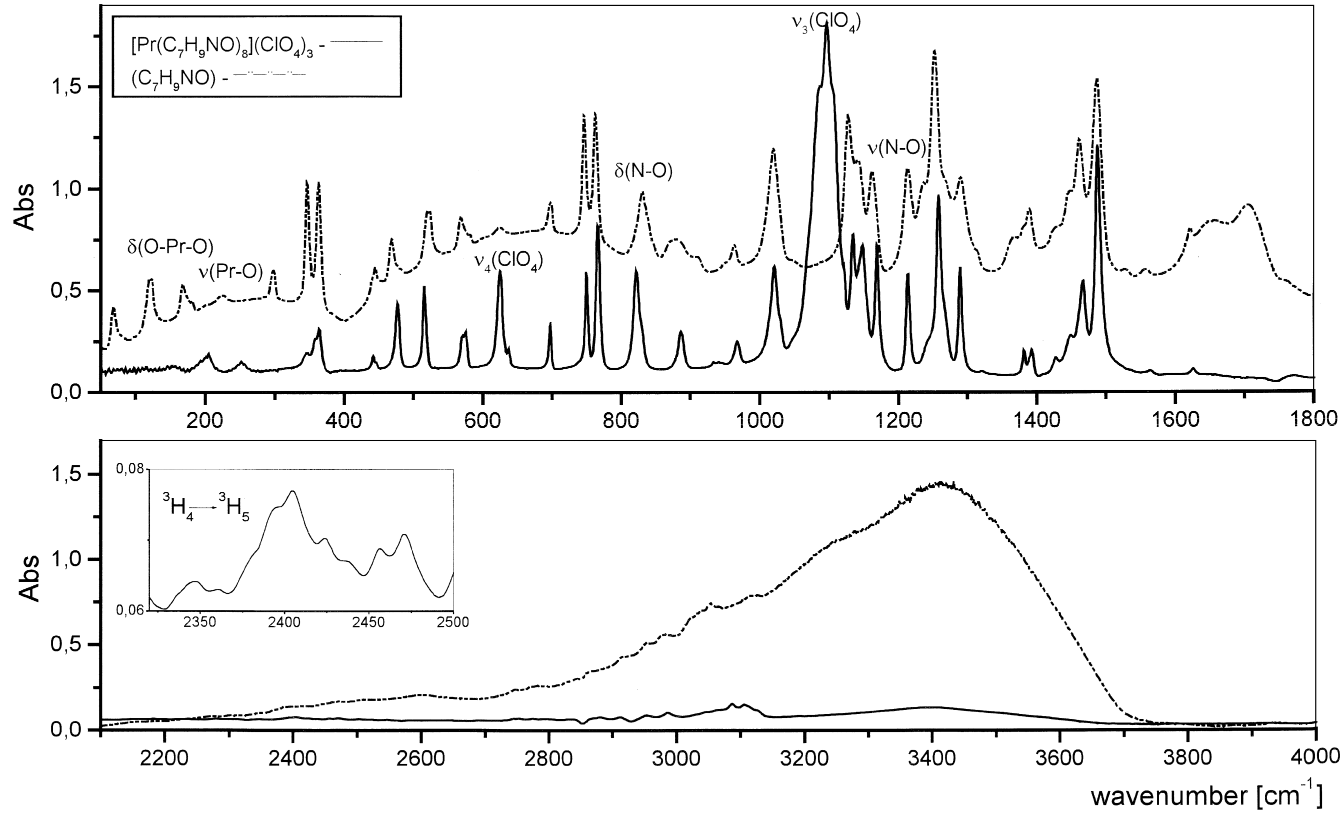

Fig. 1. IR spectra of the ligand and its praseodymium complex measured at room temperature (the inset shows the $^3H_4 \rightarrow ^3H_5$ electronic absorption transition).

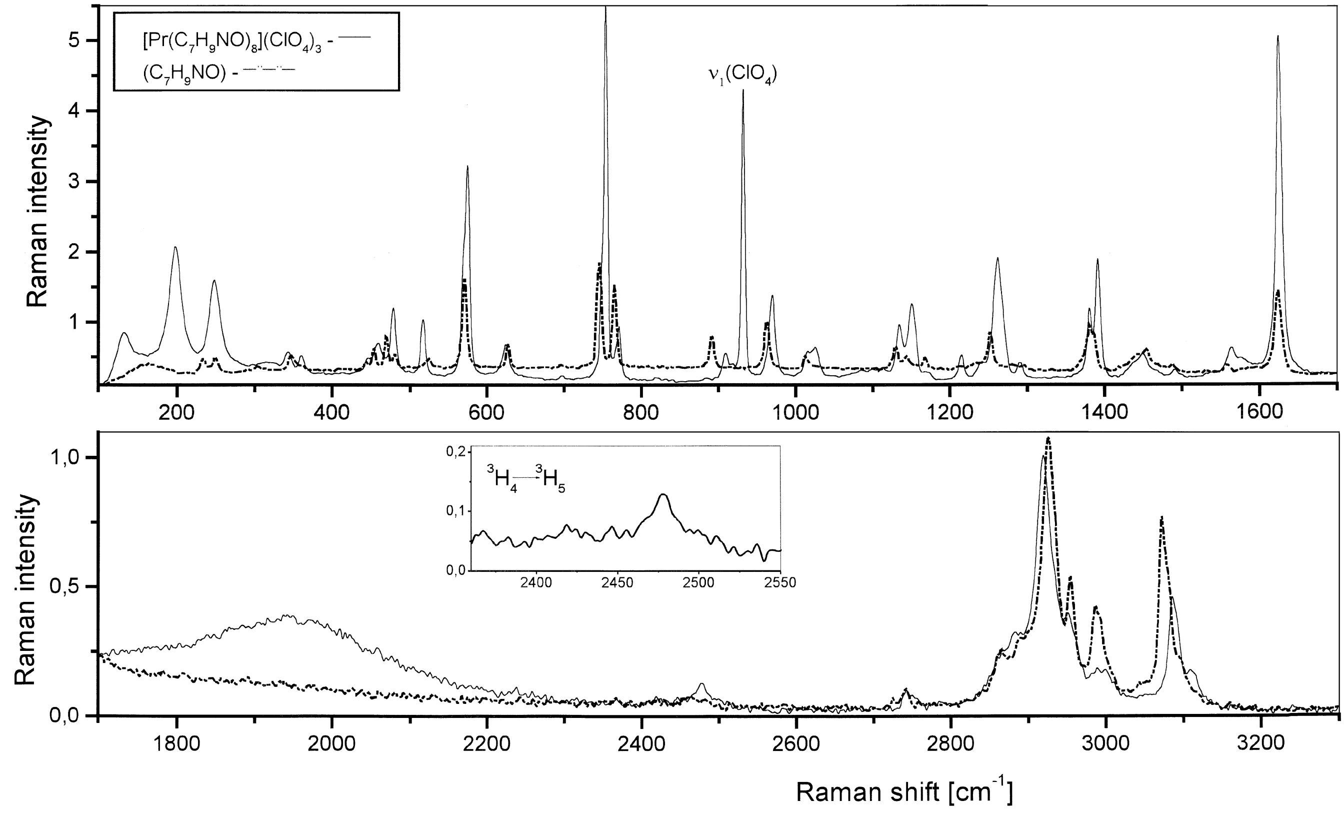

Fig. 2. Raman spectra of the ligand and its praseodymium complex measured at room temperature (the inset shows the $^3H_4 \rightarrow ^3H_5$ electronic absorption transition).

times with ethanol and dried in a vacuum apparatus over silica-gel. The yield was almost 60%. The composition was established by microanalysis giving the following stoichiometry: $[Pr(C_7H_9NO)_8](ClO_4)_3$; found: C 46.887, H 4.997, N 7.656 wt%; calculated: C 47.197, H 5.096, N 7.869 and Pr 9.896.

2.2. Spectral measurements

IR spectra were recorded in the range 10–4000 cm^{-1} in Nujol suspensions and KBr pellets using a FTIR Biorad 575C spectrometer. The resolution was 0.5 cm^{-1} in the MIR range and 1 cm^{-1} in the FIR range. Raman spectra were measured in 90° scattering geometry with a Nicolet Magna-IR 860 spectrometer. The resolution was 1 cm^{-1}. Electronic absorption spectra were recorded in the region 200–3700 nm with a Cary 5E spectrophotometer. The emission and excitation spectra were recorded on a SSF spectrofluorometer using an argon ion laser ILA 120 and a xenon lamp as excitation sources.

3. Results

3.1. IR and Raman spectra

The Fourier-transformed IR and Raman spectra of polycrystalline 2,6-lutidine *N*-oxide and its praseodymium(III) perchlorate octakis complex are presented in Figs. 1 and 2. Assignment of most of the observed bands is straightforward and achieved simply by making a comparison between the ligand and its complex

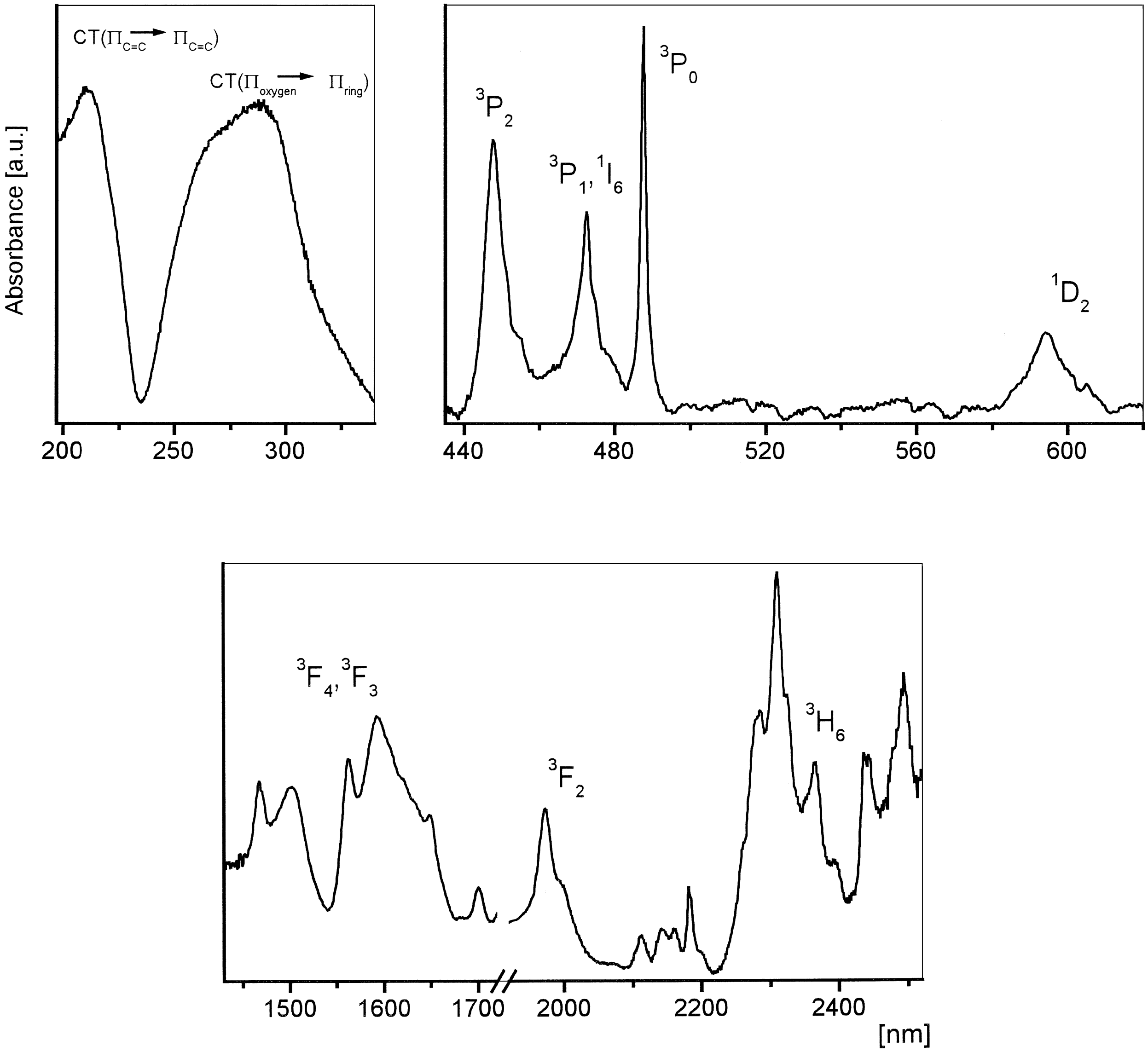

Fig. 3. Electronic absorption spectrum of the complex studied (the transitions are from the $^3H_4$ ground state to the [SL]J states) obtained at room temperature.

spectra. The description of the bands is based on our previous work concerning the vibrational behaviour of pyridine *N*-oxides [6–9]. The vibrational modes characteristic for the compounds studied are observed in the following frequency regions: ν(N–O) 1216(IR), δ(N–O) 830(IR), $\nu_1(ClO_4)$ 932(RS), $\nu_3(ClO_4)$ 1099(IR) and $\nu_4(ClO_4)$ 624(IR) cm^{-1}. The IR bands in the 200–255 region and at about 150–170 cm^{-1} correspond to the stretching and bending ν(Pr–O) and δ(O–Pr–O) vibrations, respectively. All these bands are shown in Figs. 1 and 2. It should be noted that no bands were observed in the regions characteristic for the water molecule. This means that neither coordinated nor lattice water is present in the complex studied.

3.2. Electronic absorption and emission spectra

The electronic absorption, emission and excitation spectra of the complex under investigation are presented in Figs. 3 and 4. The spectra measured at 300 and 77 K are virtually identical. This is due to the fact that these studies were performed for the polycrystalline state only because single crystals are not yet available. Although these spectra should be more resolved at 77 K, the temperature effect was compensated by the worse measurement conditions in the low-temperature cryostat.

The absorption spectra in the UV region consist of two strong, broad bands at about 47,620 and 35,400 cm^{-1}. These correspond to the charge transfer $\pi_{C=C}\rightarrow\pi_{C\cdots C}$ and $\pi_{oxygen}\rightarrow\pi_{ring}$ transitions, respectively [10]. They can be used for the population of the lowest triplet level before the ligand-to-metal energy transfer occurs. These bands are characteristic of a wide class of pyridine *N*-oxide derivatives [11]. They cover the f–d charge transfer transitions of Pr^{3+} which have significantly lower intensity.

In the visible region, the multiplet typical for Pr^{3+} is observed. It corresponds to the transitions from the ground state to $^3P_2$ (22,341 cm^{-1}), $^1I_6+{}^3P_1$ (21,186 cm^{-1}), $^3P_0$ (20,509 cm^{-1}), $^1D_2$ (16,812 cm^{-1}), $^3F_{4,3}$ (6387 cm^{-1}), $^3F_2$ (4983 cm^{-1}) and $^3H_6$ (4207 cm^{-1}) levels. These lines are strong and narrow and their shape suggests the appearance of Pr^{3+} in the single crystallographic site. The position of the $^3H_4\rightarrow{}^3H_5$ transition was obtained from the IR and Raman spectra. It appears at 2425 cm^{-1}.

The luminescence measurements indicate that this material is highly luminescent, exhibiting a band intensity two

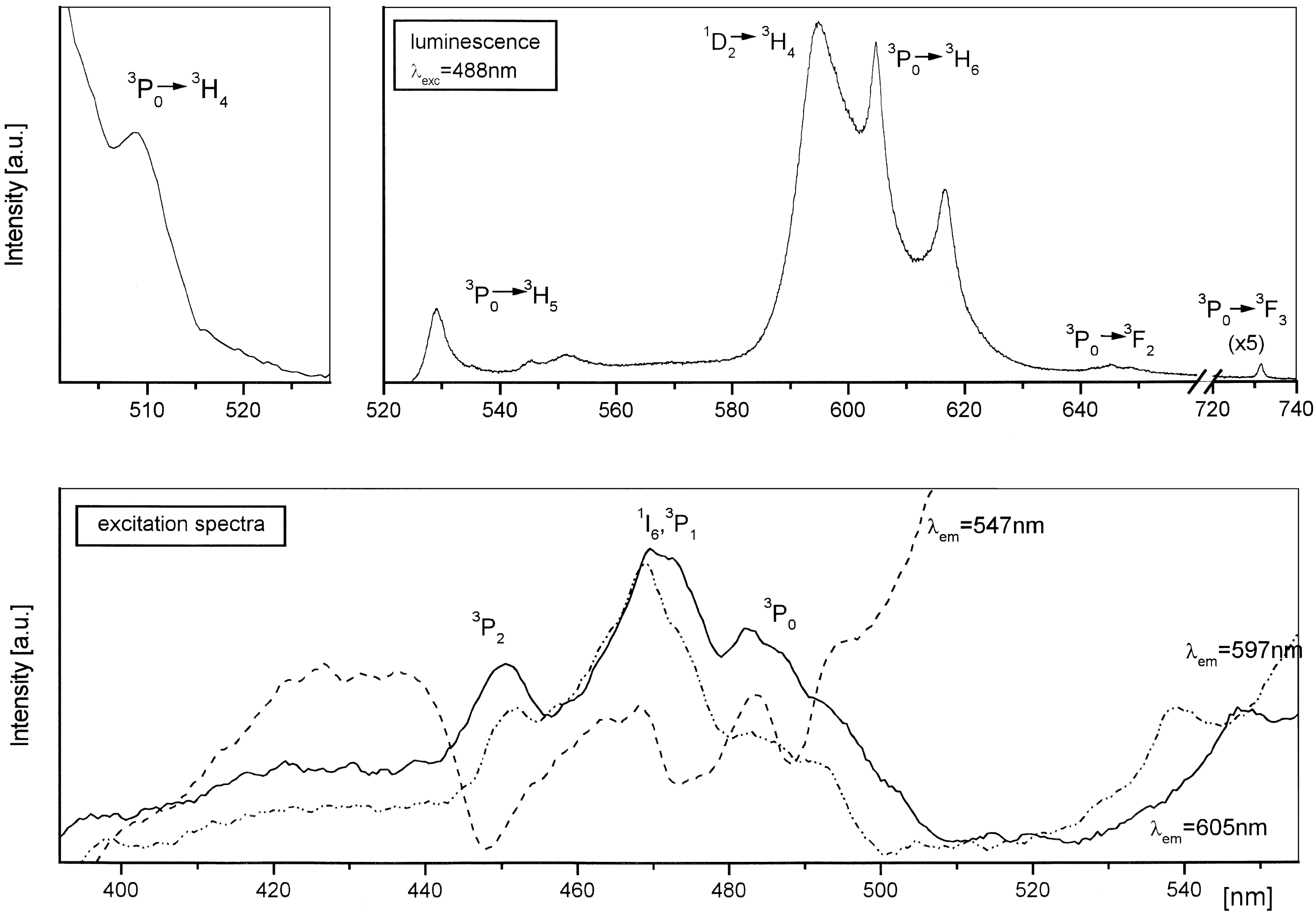

Fig. 4. Emission and excitation spectra of the complex studied measured at 300 and 77 K and obtained with several λ_{exc} lines.

orders of magnitude stronger than those observed for compounds with other Pr/ligand ratios [12]. The emission is concentrated in the red region, although the visible components also have large intensity. The following transitions are observed: $^3P_0 \rightarrow ^3H_5$ (18,350, 18,150 cm^{-1}), $^1D_2 \rightarrow ^3H_4$ (16,800, 16,530 cm^{-1}), $^3P_0 \rightarrow ^3H_6$ (16,210 cm^{-1}), $^3P_0 \rightarrow ^3F_2$ (15,500, 15,400 cm^{-1}), $^3P_0 \rightarrow ^3F_3$ (13,660 cm^{-1}).

The excitation spectra were recorded using $\lambda_{em} = 547$, 597 and 605 nm. In all cases the same $^3P_{1-3}$ multiplet was observed. This result, displayed in Fig. 4, shows that Pr^{3+} occupy one cationic site. The lifetimes of the $^3P_0$ and $^1D_2$ states were obtained at 298 and 77 K by monitoring the 547 nm line of the $^3P_0 \rightarrow ^3H_5$ emission and the 595 nm line of the $^1D_2 \rightarrow ^3H_4$ emission. The excitation used was the 487 nm line of an excimer laser. The values obtained were $\tau = 490$ and 504 ns for the former and $\tau = 224$ and 568 ns for the latter transition, for 298 and 77 K, respectively.

4. Conclusions

Table 1 compares the spectroscopic data for two types of praseodymium(III) complexes with lutidine *N*-oxides, octa- and hexa-coordinate. The PrL_8 and $PrCl_3L_2(H_2O)$ complexes differ in the coordination number and Pr/L ratio. The spectroscopic behaviour of both systems is quite similar, however the intensities of the electron bands in the absorption and emission spectra are significantly greater for the PrL_8 complexes. In addition, in the hexacoordinate complexes the praseodymium ions occupy two crystallographic sites. This leads to the splitting of some bands or their broadening. This work indicates that, among the complexes formed by praseodymium(III) and lutidine *N*-oxide ligands, the octakis compounds seem to be the most promising luminescence materials. They can easily be excited within the absorption bands belonging primarily to the ligands. The resonance with the excited levels of the lanthanide ion is quite good and should therefore lead to increased luminescence efficiency, necessary in light-conversion molecular devices.

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Table 1
Comparison of the spectroscopic data for $[PrL_8]$ and $[PrCl_3L_2(H_2O)]$ type compounds (level energies are in cm^{-1})

	$[Pr(C_7H_9N)_8]ClO_4$	$[PrCl_3(H_2O)(BrC_7H_8NO)_2]H_2O$ [4]
Electronic levels		
$^3P_2$	22,831–21,739	23,256–22,026
$^3P_1 + ^1I_6$	21,739–20,704	22,026–20,964
$^3P_0$	20,704–20,202	20,964–20,284
$^1D_2$	17,361–16,260	17,391–16,420
$^1G_4$		10,309–9328
$^3F_4$,$^3F_3$	6944–5831	7375–5865
$^3F_2$	5181–4785	5341–4728
$^3H_6$	4274–4141	4600–4241
$^3H_5$	2340–2490	
Vibrational levels		
ν(N–O)	1122,1135, 1169,1214 (IR), 1221,1237, 1272 (RS)	1223, 1270,1280 (IR), 1221,1237, 1272 (RS)
δ(N–O)	515, 624 (IR), 542 (RS)	546, 812 (IR), 542 (RS)
ν(Pr–O)	204 (IR)	182, 213, 235 (IR), 178, 200, 223 (RS)
δ(O–Pr–O)	134 (RS)	128 (IR), 134 (RS)
Lifetime		
$^3P_0$ state	$\tau = 490$ ns (300 K) $\tau = 504$ ns (77 K)	$\tau_1 = 150$ ns, $\tau_2 = 615$ ns (300 K)
$^1D_2$ state	$\tau = 224$ ns (300 K) $\tau = 568$ ns (77 K)	$\tau_1 = 110$ ns, $\tau_2 = 555$ ns (300 K)

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