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Lanthanide complexes with diethyl(2-oxopropyl) phosphonate and diethyl(2-oxo-2-phenylethyl) phosphonate ligands

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Abstract

Ln^{3+} complexes with the phosphonate ligands: diethyl(2-oxopropyl) phosphonate $[CH_3C(O)CH_2P(O)(OC_2H_5)_2]$ (OPP) and diethyl (2-oxo-2-phenylethyl) phosphonate $[C_6H_5C(O)CH_2P(O)(OC_2H_5)_2]$ (DEPP) were synthesized and characterized. Complexation studies and spectral characterizations are performed. Based on the Nd^{3+} absorption spectra, using computer-assisted target factor analysis, the stability constants of Nd-OPP complexes in solution were determined to be $\log \beta_{11} = 2.8 \pm 0.4$ and $\log \beta_{12} = 5.0 \pm 0.7$. Luminescence intensities, lifetimes, τ, and quantum yields, Φ, of the Eu^{3+} and Tb^{3+} ions in the complexes were measured. The most intense luminescence was observed in the case of the Tb/DEPP system. Emission enhancements were observed for Tb^{3+} and Eu^{3+} complexes in acetonitrile solutions, which occurred as a result of sensitized luminescence. These observed luminescence intensities were over two orders of magnitude larger than those for the uncomplexed Ln(III) ions.

The complexes of $Ln/L/NO_3$, obtained in oil forms from ethanol at room temperature, were characterized by elemental analysis, IR spectroscopy, and luminescence lifetime measurements. The composition of the complexes studied is suggested to be $LnL_2(NO_3)_3$, with monodentate coordination by the phosphoryl group.

Keywords: Absorbance; Lanthanide ions; Luminescence; Phosphonate ligands

1. Introduction

Phosphonates are important in biology and in living systems as effective complexing agents [1]. Their complexes with Ln^{3+} ions have been extensively investigated with regard to their structures and their various practical applications [2–4]. A series of lanthanide phosphonate complexes, containing P=O and O=C–N groups, closely related to β-diketones, have been used for the extraction and separation of these ions [5,6]. Ln(III) compounds type of phosphoro-azo derivatives of the β-diketones undoped and doped with αα′dipyridyl have been recently reported in [7], and the interactions of the ligands with the lanthanide ions were confirmed both by IR and electronic spectra. The synthesis, structures, and catalytic behavior of the complexes bis(diphenylphosphino)methane dioxide $[Ph_2P(O)CH_2P(O)Ph_2]$ with $Ln(OTf_3)_3$ [8] and $Ln(NO_3)_3$ [9] have been studied. Complexes of $(EtO)_2P(O)CH_2P(O)(OEt)_2$ with lanthanide nitrates have also been characterized, and their stable compositions as $LnL_2(NO_3)_3$ were isolated for the lanthanides series La–Eu. [10].

The purpose of this work is to characterize the complexes of the OPP and DEPP ligands with lanthanide nitrates in acetonitrile solution and in oil forms, using complexation studies and spectroscopic characterizations.

2. Experimental

The $Ln(NO_3)_3$ salts were obtained by dissolving lanthanide oxides (spectroscopically pure, prepared in Laboratory of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University, Poznań) in nitric acid (p.a.). Stock solutions for the spectroscopic study were prepared by dissolving them and the ligands in acetonitrile (Aldrich, 99.93%). The commercially available ligands: diethyl(2-oxopropyl) phosphonate and diethyl(2-oxo-2-phenylethyl) phosphonate (Aldrich) were used without further purification (Fig. 1).

The 1:2 complexes were prepared by mixing together stoichiometric quantities of lanthanide nitrates and $R–C(O)CH_2P(O)(OEt)_2$ (where $R = CH_3$ or C_6H_5) in ethanol. The reaction mixtures were stirred for 1 h at room temperature. The solvent was evaporated in air, and the oil products were washed with isopropanol and dried under vacuum.

The absorption spectra of Nd^{3+} complexes were measured on a Shimadzu UV-2401 PC spectrophotometer and used for the threshold bootstrap computer-assisted target factor analysis (TB CAT) previously described in [11]. The spectra

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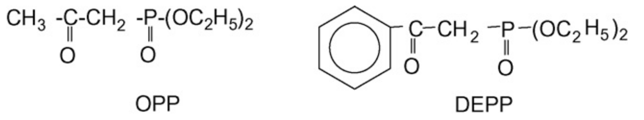

Fig. 1. Structures of the studied ligands.

of sample acetonitrile solutions with varying molar ratios of the components were recorded with spectral slits of 0.5 nm and with 0.2 nm steps using cuvettes having 4 cm path lengths. Four repeated scans were averaged to reduce the spectral noise. Interactions of Nd^{3+} with the OPP ligand were studied using the absorption bands at 550–615 and 705–773 nm corresponding to the transitions $^4I_{9/2}$–$^4G_{5/2}$,$^2G_{7/2}$ ($\lambda_{max} \sim 581$ nm) and $^4I_{9/2}$–$^4F_{7/2}$,$^4S_{3/2}$ ($\lambda_{max} \sim 736$ nm). Luminescence measurements were made on a Perkin Elmer MPF3 spectrofluorimeter. All samples were prepared by mixing appropriate amounts of Eu^{3+} or Tb^{3+} and the ligands in scaled flasks of 5 ml volume. The luminescence lifetime and excitation spectra of the $^5D_0$–$^7F_0$ transition of Eu^{3+} were measured using a detection system, consisting of a nitrogen laser pumping a tunable dye laser (using the P3 CDOMAT dye in acetonitrile), as described previously in ref. [12]. Experiments were conducted at room temperature.

The IR spectra of the ligands and complexes were recorded on a Bruker infrared spectrophotometer IFS 66v/S using the KBr pellet technique. The elemental analyses of the complexes were carried out with an elemental analyzer, VARIO EL III, Elementar. Experimental data were in good agreement with the theoretical values; found: C, 23.66; H, 4.63; N, 5.81; calculated: C, 23.57; H, 4.21; N, 5.89; for $LaL_2(NO_3)_3$ where L is OPP, and found: C, 36.89; H, 4.55; N, 4.28; calculated: C, 35.30; H, 4.57, N, 4.57% for $TbL_2(NO_3)_3.C_3H_8O$ where L is DEPP. ^{13}C and ^{31}P NMR spectra were recorded on a VARIAN Mercury 300 in 5 mm tubes at room temperature. The spectra were referenced to the corresponding solvent signals (^{13}C) or externally to 85% aqueous H_3PO_4 (^{31}P).

3. Results and discussion

The Nd(III) absorption spectra of the systems showed a deceasing of the molar absorption coefficients, ε, and a bathochromic shift of absorption bands with the addition of the ligand, as presented in Fig. 2. The bands $^4I_{9/2}$–$^4G_{5/2}$, $^2G_{7/2}$ ($\lambda_{max} \sim 581$ nm) and $^4I_{9/2}$–$^4F_{7/2}$, $^4S_{3/2}$ ($\lambda_{max} \sim 736$ nm), showing the largest changes after ligand addition, were analyzed using the TB CAT [11]. This analysis (30 experimental spectra) revealed the existence of two species ML and ML_2 of the Nd/OPP complexes. Their stability constants were calculated as $\log\beta_{11} = 2.6 \pm 0.4$ and $\log\beta_{12} = 4.9 \pm 1.0$ for the $^4I_{9/2}$–$^4G_{5/2}$, $^2G_{7/2}$ transition and $\log\beta_{11} = 2.9 \pm 0.5$ and $\log\beta_{12} = 4.7 \pm 0.6$ for the $^4I_{9/2}$–$^4F_{7/2}$,$^4S_{3/2}$ transition, respectively. The $\log\beta$ values obtained from measurements concerning the combined Nd^{3+} spectra were as follows: $\log\beta_{11} = 2.8 \pm 0.4$ and $\log\beta_{12} = 5.0 \pm 0.7$, respectively.

Fig. 3 shows the absorbance and excitation spectra for the Tb/DEPP system. The absorption spectra of the ligands, under study (also their complexes with Eu^{3+} and Tb^{3+} ions) showed one or two bands at about 210 and 260 nm, respectively, in the range 200–400 nm. No significant bathochromic shifts were observed upon complexation.

All excitation spectra were recorded by monitoring the Eu(III) luminescence at 618 nm and the Tb(III) luminescence at 548 nm. The complexes of Eu^{3+} and Tb^{3+} are characterized by similar excitation spectra and have the same maximum in their respective excitation spectra. Excitation of the Eu^{3+} and Tb^{3+} systems at $\lambda = 270$ nm in CH_3CN solutions resulted in characteristic emissions with the following transi-

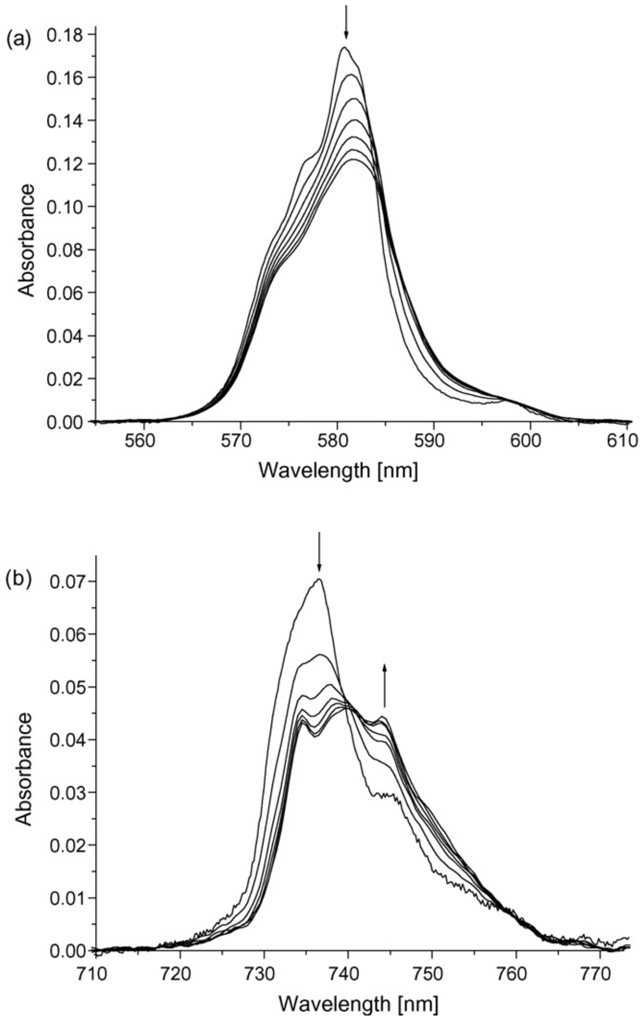

Fig. 2. The absorption spectra of Nd^{3+} ion, in Nd(III)-OPP system (molar ratio from 1:0 to 1:6) in range of $^4I_{9/2}$–$^4G_{5/2}$, $^2G_{7/2}$ (a) and $^4I_{9/2}$–$^4F_{7/2}$, $^4S_{3/2}$ (b) transitions.

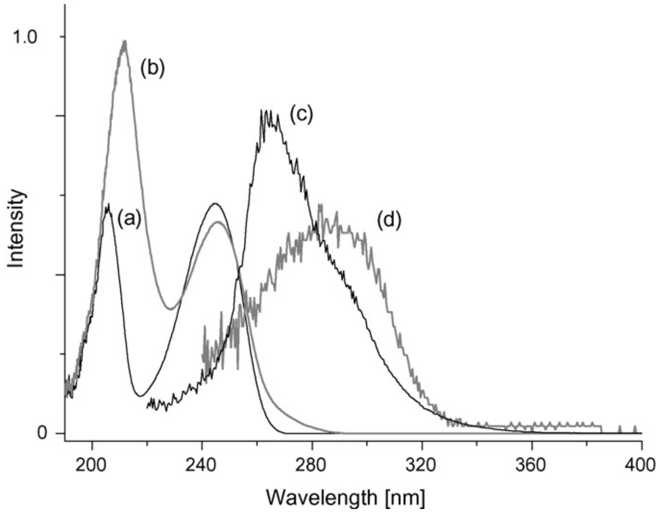

Fig. 3. Absorption spectra of DEPP (a), and Tb-DEPP (b), and excitation spectra of Tb-DEPP (c) and Tb-OPP (d) recorded in CH_3CN solution.

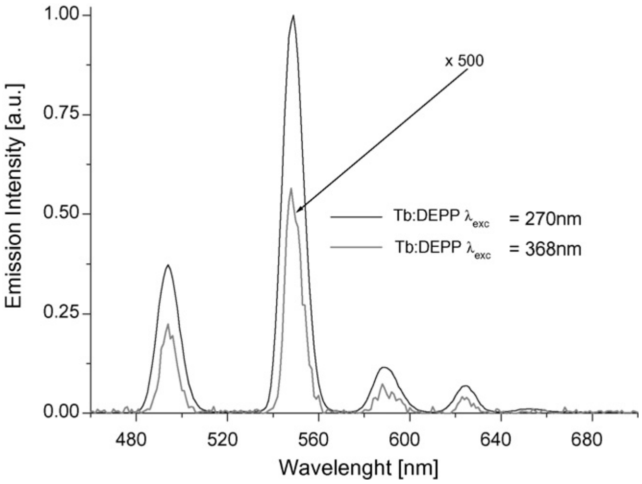

Fig. 4. Emission spectra of the Tb/DEPP (1:3) systems in CH_3CN solution, $C_{Tb^{3+}} = 4 \times 10^{-5}$ M.

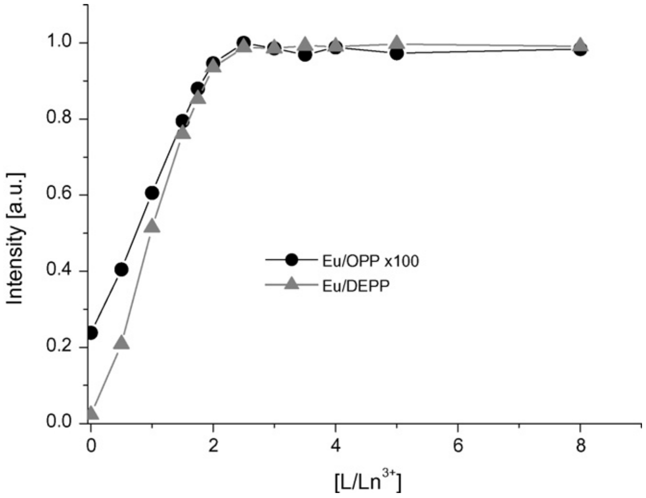

Fig. 5. Plots of the Eu^{3+} luminescence intensity vs. [L/Ln^{3+}] in the Eu^{3+}/L (L = OPP and DEPP) systems.

Table 1
The luminescence parameters for the Eu^{3+} and Tb^{3+} systems

System (1:3 molar ratio)	λ_{ex} (nm)	I_{lum}	Φ_{lum} (%)[a]
Eu/OPP	300	0.04	–
Eu/DEPP	270	0.45	7.7
Tb/OPP	300	0.09	–
Tb/DEPP	270	1	11.1

[a] Excitation in the ligand absorption; $Ru(byp)_3{}^{2+}$ ($\Phi = 0.028$ in aerated water) and quinine sulphate ($\Phi = 0.577$ in 0.1 M H_2SO_4).

tions: $\lambda = 595$ nm ($^5D_0$–$^7F_1$), 618 nm ($^5D_0$–$^7F_2$), and 697 nm ($^5D_0$–$^7F_4$) for europium, and $\lambda = 493$ nm ($^5D_4$–$^7F_6$), 548 nm ($^5D_4$–$^7F_5$) 589 nm ($^5D_4$–$^7F_4$), and 625 ($^5D_4$–$^7F_3$) for terbium. As shown in the spectra (Fig. 4), for the terbium ion, the most intense emission can be attributed to the $^5D_4$–$^7F_5$ transition. For the europium ion, the $^5D_0$–$^7F_2$ transition was the most intense.

The spectra of the Eu–L and Tb–L complexes formed in the acetonitrile solution showed a large increase in the Ln(III) luminescence for the M:L 1:2 molar ratio (Fig. 5). The intensities of the DEPP complexes were larger than those of the OPP complexes (Table 1). At 394 and 368 nm excitation, the Eu–L and Tb–L systems showed very weak luminescence (Fig. 4).

This very weak luminescence of the Eu^{3+} and Tb^{3+} ions, together with the observed excitation spectra (Fig. 3), indicates that the enhanced Eu^{3+} and Tb^{3+} emission observed in the complexes under study were due to energy transfer from the ligands to the Ln^{3+} ions (antenna effect). The energy transfer was more effective for the Tb^{3+} complexes compared to that in the Eu^{3+} complexes. The luminescence quantum yields of the complexes (Table 1) were measured [13] using $Ru(byp)_3{}^{2+}$ ($\Phi = 0.028$ in water) and quinine sulphate ($\Phi = 0.577$ in 0.1 M H_2SO_4) as standards [14,15]. Following the trend in the emission spectra, the quantum yield for the Tb^{3+} complex was much higher than the corresponding value for the Eu^{3+} complex.

The selective excitation spectra of $^5D_0$–$^7F_0$ of europium ion were measured. The ground state and the excited state are nondegenerate. Since the ligand field cannot further split these states, only a single electronic transition is allowed for each Eu^{3+} environment. The excitation spectra for different molar ratios of $Eu(NO_3)_3$ and DEPP in CH_3CN are shown in Fig. 6.

Deconvolution of the spectra shows peaks with maxima at 579.16 (free metal ion), 579.55 (M:L 1:1), 579.98 (M:L 1:2, 1:3,), and 580.02 nm (1:4). The luminescence decay times were obtained by fitting the decay curves, from the maxima, to a single exponential function. For the free Eu^{3+} (as $Eu(NO_3)_3$) in CH_3CN solution, the luminescence exhibited a faster decay with a lifetime of 468.3 μs. The 1:1 Eu/DEPP system showed a luminescence lifetime equal to 958.1 μs. The luminescence measured

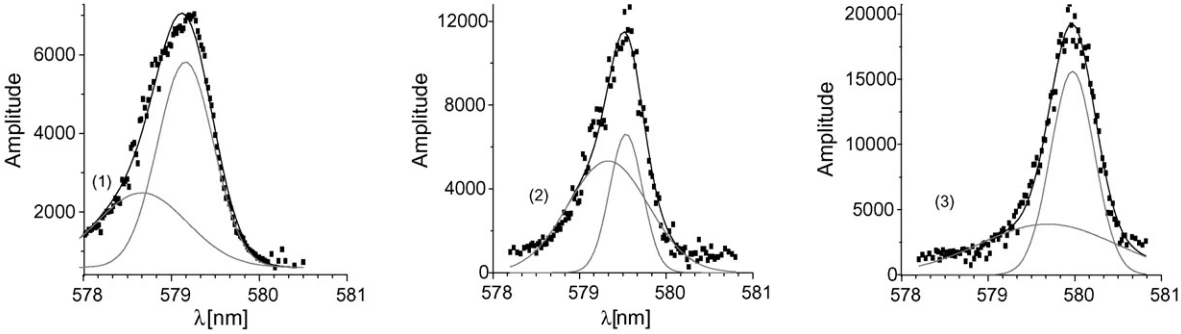

Fig. 6. The Eu^{3+} selective excitation spectra in the range of $^7F_0$–$^5D_0$ transition recorded in room-temperature for various Eu/DEPP ratios, $C_{Eu^{3+}} = 0.001$ M; Eu^{3+}/L = 1:0 (1), 1:1 (2), 1:2 (3).

Table 2
The IR data for the OPP and DEPP ligands and their complexes with La^{3+} and Tb^{3+} ions

Ligand OPP		La/OPP system		$\Delta\nu$
1716	C=O	1721.8	C=O	+5.8
1257.9	P=O	1204.6	P=O	−53.3
–		2522.1 w	NO_3 ν_{1+3}	+213.3
–		2308.8 w	NO_3 ν_{1+3}	
–		2058.2 v.w	NO_3 $2\nu_1$	
–		1982 v.w	NO_3 $2\nu_1$	
–		1498 s	NO_3 ν_3	+189.3
–		1308.7 s	NO_3 ν_3	
–		817.5 m	NO_3 ν_2	
–		743.2 m	NO_3 ν_4	+37.1
		706.1 v.w	NO_3 ν_4	
1052.3	P–O–C	1049.0	P–O–C	−3.3
1026.5	P–O–C	1029.8	P–O–C	+3.3
821.1	P–O–C	828.2	P–O–C	+7.1
1444.5	C–P	1446.4	C–P	+1.9
789.3	C–P	796.7	C–P	+7.4
771.9	C–P	770.2	C–P	−1.7
Ligand DEPP		**Tb/DEPP system**		$\Delta\nu$
1681.6	C=O	1683.7	C=O	+2.1
1253.8	P=O	1184.5	P=O	−69.3
–		2519.1 w	NO_3 ν_{1+3}	+214.4
–		2304.7 w	NO_3 ν_{1+3}	
–		1979.6 v.w	NO_3 $2\nu_1$	
		1771.3 v.w	NO_3 ν_{1+4}	
–		1494.5 s	NO_3 ν_3	+194.8
–		1299.7 s	NO_3 ν_3	
–		816.4 m	NO_3 ν_2	
–		743 m	NO_3 ν_4	+38.4
		704.6 v.w	NO_3 ν_4	
1054.4	P–O–C	1051.5	P–O–C	−3.3
1026.6	P–O–C	1029.7	P–O–C	+3.1
836.2	P–O–C	841.6	P–O–C	+5.2
1448.7	C–P	1449.2	C–P	+0.5
785.4	C–P	774.7	C–P	−10.7
751.8	C–P	743.2	C–P	–8.6

for the 1:2 and 1:3 systems exhibited exponential decays with lifetimes of equal to 1145.5 and 1177.2 μs, respectively. For the 1:4 system, the luminescence lifetime was determined to be 1205.1 μs. This confirms that the ML and ML_2 complexes were formed in acetonitrile solutions.

The IR spectra of the free ligands and their coordination compounds were recorded. The main changes in the spectra were related to the ν(NO) and ν(PO) bands. The IR spectra of the free ligands and their complexes, in KBr tablets, contained absorption bands at 1253–1258 and 1184–1204 cm^{-1}, respectively, due to the P=O valence vibrations (Table 2). The lower ν(PO) frequencies of the complexes compared with analogous frequencies of the ligands ($\Delta\nu(PO) = 53–69\,cm^{-1}$) support the notion that coordination is via the phosphoryl oxygen atom. This is in agreement with the data for other lanthanide complexes [16,17].

The IR spectrum of the nitrate ion shows bands: ν_2 (out-of-plane deformation), ν_3 (doubly degenerate stretch), ν_4 (doubly degenerate in-plane bending), and combination bands: $\nu_1 + \nu_3$ and $\nu_1 + \nu_4$ [18]. Methods to discriminate between ionic, bidentate, and monodentate nitrate groups have been reported [18–20]. The presence, in the studied complexes, of the bands for ν(NO) around 2300–2520, 1300–1500, and 700–740 cm^{-1}, in addition to the high values of $\Delta\nu_3$ (∼200 cm^{-1}) and $\Delta\nu_4$ (∼40 cm^{-1}, Table 2), can be taken to be an indication of the bidentate nature of the nitrate ion. This is in accord with the data for alternative complexes [10,17].

The ligands under study, contained intense C=O vibrational peaks at 1716 and 1682 cm^{-1} for the OPP and DEPP ligands, respectively. The absence in the IR spectra of a low-frequency shift in the C=O bands suggests that there is coordination only by the P=O groups in the systems studied.

The $La(OPP)_2(NO_3)_3$ complex is diamagnetic. Table 3 shows the chemical shifts in the ^{13}C and ^{31}P NMR spectra of solutions of the OPP ligand and the $La(OPP)_2(NO_3)_3$ complex in CD_3OD. The ^{31}P NMR spectrum of the complex exhibits one singlet, indicating the homogeneity of sample.

In the ^{13}C NMR spectrum of the $La(OPP)_2(NO_3)_3$ complex, there was a significant shift of the signals associated with the carbon atom directly bonded to the phosphorus atom (CH_2–P), but there was no change of the position of the signal due to the carbon atom of the CO group. This indicates there is direct participation of the PO group in the coordination of the La^{3+} ion, and it confirms the results from the IR spectra indicating that the ligands under study are monodentate.

4. Conclusion

We have performed a detailed study of the spectroscopic properties of lanthanide(III) ions with the organophosphorus ligands, OPP and DEPP. In solution, the ligands form M:L and M:L_2 complexes with the Ln^{3+} ions. The excitation and emission spectra show that energy transfer from the ligands to the Eu^{3+} and Tb^{3+} ions occurred.

Counter ions can play a significant role in the formation of complexes of the type $LnL_2(NO_3)_3$. Based on the infrared and NMR spectra (^{13}C and ^{31}P) one can conclude, that the phosphoryl groups of the two organophosphorus ligands and three NO_3^- ions, which act as bidentate ligands, chelate the lanthanide ions.

Table 3
NMR data for the OPP ligand and $La(OPP)_2(NO_3)_3$ complex in CD_3OD solution

	Compounds					
	$\delta(^{31}P)$	$\delta(^{13}CH_3CO)$	$\delta(^{13}C{=}O)$	$\delta(^{13}CH_2P)$	$\delta(O^{13}CH_2)$	$\delta(CH_2{}^{13}CH_3)$
Ligand	20.87	31.52	201.59	42.15, 43.86	64.10	16.64
Complex	21.32	31.58	202.19	58.34	64.44	16.57

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