Complexes of Esters of Ethylenediphosphonic Acid with Lanthanide Nitrates—Synthesis and Structure

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ABSTRACT: *The lanthanide complexes $L_2Ln(NO_3)_3$ (3) and $L'_3[Ln(NO_3)_3]_2$ (5) (Stewart and Siddall III. J Inorg Nucl Chem 1971, 33, 2965–2970) were obtained, where L is the tetraethyl ester of ethylenediphosphonic acid (2), L' is the tetraisopropyl ester of ethylenediphosphonic acid (4), and Ln is La, Ce, Sm, Eu, and Er. In extension of a former study, they were characterized additionally with NMR spectroscopy. In contrast to the compounds of type 3, the erbium complex of the ligand L is consistent with the formula $L_3[Er(NO_3)_3]_2$. The crystal structure of the complex 3a (Ln = La) is determined by single crystal X-ray diffraction. The complex is found to crystallize in the monoclinic space group C2/c with a = 15.1415(4) Å, b = 14.9749(4) Å, c = 18.3887(5) Å, β = 114.129(1)°, T = 153 K, V = 3805.2(2) Å³, Z = 4, ρ_{calc} = 1.622 g/cm³, R_1 = 0.023, R2w = 0.058, S = 1.08 for all 6823 reflections. The complex 3a consists of polymer chains with bridged bidentate phosphonate ligands. The lanthanum atom is coordinated by ten oxygen atoms, six of them from the three bidentate nitrate ions, and four from the two phosphonate ligands.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:36–46, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20188

INTRODUCTION

Diphosphonates have wide applications in the practice. They are clinically used as drugs for various calcium-related disorders such as tumor osteolysis and osteoporosis [2–5], some of them are thought to be useful as anti-inflammatory and antiarthritic compounds [6]. Ethylene diphosphonate ligands, containing two P=O groups as coordinated centers, are widely used for extraction of actinides and europium [7–11]. Their complexes with Sb, Sn, and Ti are useful as fire retardants for polymers [12]. The complexes of esters of ethylene- and propylene-diphosphonic acids with uranium (III) [7] or tin [13] containing salts, as well as with molybdenum dioxodichloride [14], are isolated and characterized.

Recently we described the synthesis and structure of complexes of lanthanide nitrates with some carbamoylphosphonates, where the coordination is realized by both the phosphoryl and amide-carbonyl oxygen atoms as a stable chelate [15]. It was interesting to extend these studies to the complexation of these nitrates by diphosphonates, containing two methylene groups. It is known that when the coordinating chelate becomes bigger (seven or more members) the probability increases for a linear or another

kind of coordination. In the present work, we have studied the coordination of the tetraethyl esters and augment studies of the tetraisopropyl esters [1] of ethylenediphosphonic acid (**2** and **4**) by lanthanide nitrates (**1**).

RESULTS AND DISCUSSION

Complexes of the Tetraethyl Ester of Ethylenediphosphonic Acid (L) with Lanthanide Nitrates

The coordination of the tetraethyl ester of ethylenediphosphonic acid **2** (L) with lanthanide nitrates **1a–e** was performed in ethanol at room temperature. The reaction was carried out for 30 min at a ligand/nitrate ratio of 2:1. In all cases the complexes **3a–e** are formed according the Scheme 1.

After washing of the crude product with ethanol/ether mixture and then with ether, white crystalline products **3a–d** and rose **3e** were isolated in 60–84% yield. Their solubility is described in the Experimental.

The elemental analysis confirmed the ligand/lanthanide ratio 2:1 for the complexes **3a–d** ($m = 2$, $n = 1$) and 3:2 for **3e** ($m = 3$, $n = 2$).

The IR spectra in Nujol showed significant shifts of P=O and P—O—C bands to lower frequencies (see Experimental) with regard to the starting ligand **2** (νP=O 1260 cm^{-1} and νP—O—C 1035 and 1055 cm^{-1}, film). For the phosphono group, which is characterized by two or three bands in the complexes, the complexation produces low frequency shifts of 30–80 cm^{-1}, respectively. This shift is of 25 and 15–35 cm^{-1} for P—O—C bond (see Table 1).

The considerably low frequency shift is comparable to the previously obtained complexes of alkylenediphosphonic esters [1] as well as in the complexes of carbamoylmethylphosphonates with lanthanide nitrates [15–17] and is an indicatio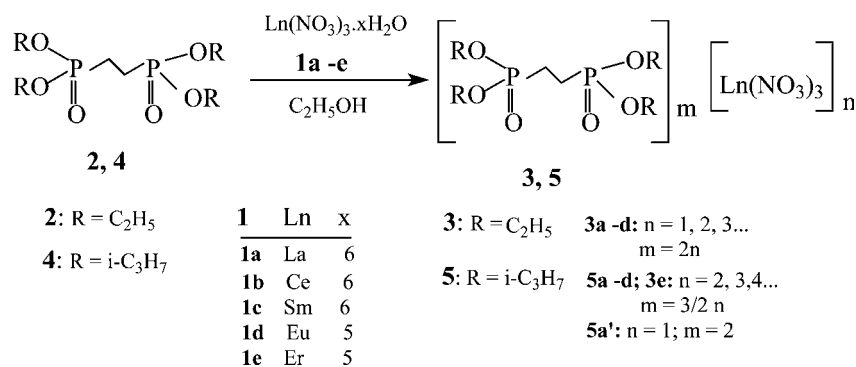n for bidentate coordination of the ligand **2**. The characterization of the nitrate group in Nujol is based on the valence frequency ν_1 [1] at about 1300 cm^{-1} (see Table 1) and is in accordance with the data for other analogous complexes [15–17]. The band ν_2 is masked behind the strong P—O—C bonding vibration, and ν_4 in **3a** and **3b** is hidden more or less by a band of Nujol (1462 cm^{-1} in KBr). Thus, they are not accessible for a reliable interpretation. In **3c–3e** the band around 1500 cm^{-1} could be assigned cautiously to ν_4.

The FT-IR spectrum of **3a** between KBr-disks contains the bands at 1484 cm^{-1}, 1446 cm^{-1}, and 1332 cm^{-1}, 1324 cm^{-1}, assigned to $\nu_{N=O}$ and ν_{NO} stretching vibrations, respectively, and supposed a bidentate coordination of the NO$_3^-$ group through its two O-atoms.

TABLE 1   IR Data in Nujol of **2** and **3a–e**

	P—O—C	P=O	NO$_3^-$
2	1035	1260	
	1055		
2[a]	1028	1246	
	1048		
3a	1021	1189 (w)	1325
	1035	1208 (s)	
		1220 (s)	
3a[a]	1021	1208	1324
	1035	1220	1332
			1446
			1484
3b	1010	1195 (m)	1330
	1030	1210 (s)	
		1225 (s)	
3c	1017 (br)	1185 (s)	1299
		1222 (s)	1514
3d	1010	1180 (s)	1300
	1020	1210 (m)	1505
3e	1010	1190 (s)	1310
	1030	1210 (m)	1500
		1230 (m)	1515

[a]In KBr; (s) strong; (m) medium; (w) weak; (sh) shoulder.

2: R = C$_2$H$_5$

4: R = i-C$_3$H$_7$

1	Ln	x
1a	La	6
1b	Ce	6
1c	Sm	6
1d	Eu	5
1e	Er	5

3: R = C$_2$H$_5$ **3a -d:** n = 1, 2, 3...
                                m = 2n

5: R = i-C$_3$H$_7$ **5a -d; 3e:** n = 2, 3,4...
                                m = 3/2 n
                          5a': n = 1; m = 2

SCHEME 1

The ^{31}P NMR spectra of **3a, 3b**, and **3c** in CD_3OD show singlets at 31.14, 40.12, and 31.18 ppm which are 1.15, 10.13, and 1.19 ppm downfield compared to the free ligand resonance (29.99 ppm). For the complexes **3d** and **3e**, only broad ^{31}P-NMR signals could be detected: **3d** at 27 ppm (linewidth = 4 kHz) and **3e** at 29 ppm (linewidth = 1.5 kHz).

The ^{1}H NMR spectra of **3a–3e** prove the ratio of protons $CH_3:CH_2-O:CH_2-P = 12:8:4$ and the ^{13}C NMR spectra (including APT-spectra for multiplicity detection) are also in accordance with the expected constitution. The ^{13}C-signals of the central $P-CH_2-CH_2-P$ moiety exhibit a five-line multiplet due to their participation in an AA'X-spin system. The appearance of the multiplet varies (Fig. 1) and may be used as an indicator for stereochemical changes during complexation, especially the $^3J_{PP}$-coupling constant. In fact, the analysis of the data show [18] that there are to some extent changes in the chemical shifts. However, while the $^1J(CP)$ and $^2J(CP)$ are only slightly affected by the complexation, the $^3J(PP)$-coupling (Table 1) changes remarkably from the free ligand to the complexes, while it remains more or less stable by variation of the lanthanoids despite **3d**. This is a strong argument for the complexation as well as a hint that there are not only electronic changes through the bonding but also stereochemical changes concerning the central PCCP unit. In general, the values are in good accordance with the literature [19]. Nevertheless, the iterative spin simulation shows that the appearance of the spectra is very sensitive to the signs and the values of the couplings, especially visible on the intensity of the central line of the multiplet. Additionally, at the given field strength (9.4 T), the spectra seem
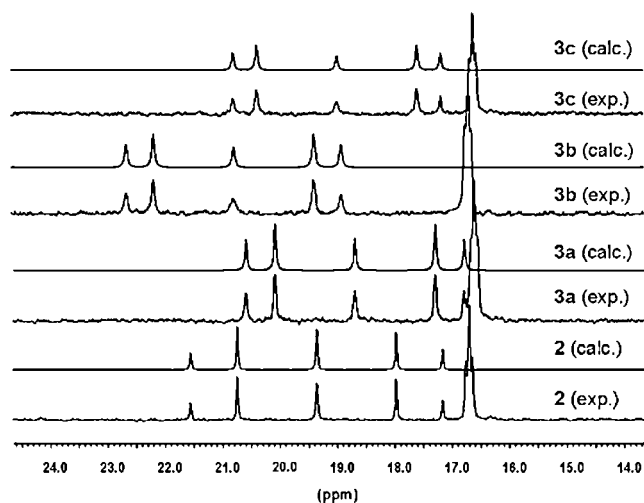
TABLE 2 ^{13}C-Chemical Shifts and Coupling Constants of the P–CH_2 group in **2** and **3a–d**

	P(A)-[13]C(X)-^{12}C-P(A')			
	δ (ppm)	J(AX) (Hz)	J(A'X) (Hz)	J(AA') (Hz)
2	19.3(5)	146.6(4)	−7.1(2)	79.3(4)
3a	18.6(9)	147.9(8)	−7.5(4)	55.8(3)
3b	20.7(7)	148.4(1)	−7.9(4)	52.3(4)
3c	18.9(7)	146.5(8)	−6.0(5)	49.4(1)
3d	18.6(5)	140.7(4)	Not obs.[a]	Not obs.[a]

The accuracy is given with respect to the calculation, not to the measurement.
[a]See Experimental.

to be "true AA'X-spectra" [20]. Manipulation of the simulated data shows that a shift difference of more than 1 Hz for the phosphorous resonances yields a detectable splitting of the central resonance, which is not observed experimentally (see Table 2). Thus, the effect of an isotopic shift of the ^{31}P frequencies due to the ^{13}C nucleus is negligible.

From the NMR data, the 2:1 ratio (ligand:lanthanoid) cannot be explained by a simple linear arrangement L–Ln–L because we only get one set of signals for all nuclei under investigation. Thus, a highly symmetric structure is expected which can be described easily like as in Fig. 2a.
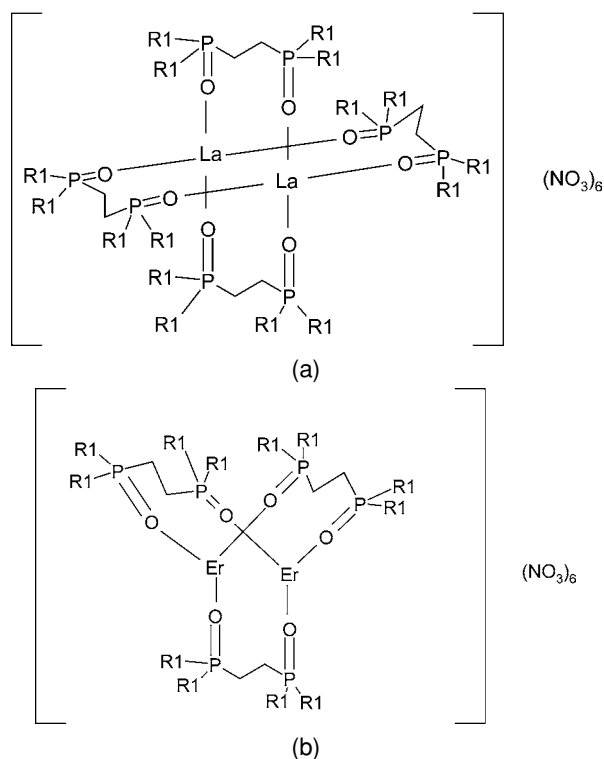

FIGURE 1 Measured and calculated ^{13}C NMR spectra of the P-CH_2-group in **2–3c**.

FIGURE 2 Schematic representation for the complexes of types **3a–3d** (a) and **3e** (b).

In this most simplified form, four ligands are bridging two lanthanoids for **3a–3d** via P=O···Ln coordination. Supporting arguments can be deduced from the ^{13}C NMR data: with the decrease in radius of the lanthanoids, the distance between the two centers is expected to decrease too and therefore the conformational rigidity around the CH$_2$—CH$_2$ moiety is increased more or less due to steric hindrance, but still yields observable intermediate couplings. Due to these data, a significant change, presumably due to the steric situation, occurs by changing to **3d**.

The flexibility around the methylene moiety is frozen, and this fixed situation yields a spectrum with the ^2J and $^3J = 0$ and an increasing linewidth of the ^{31}P-signal, both caused by increased relaxation effects due to a closer distance to the lanthanoid center. However, the situation changes dramatically from **3d** to **3e**: because of the minimum Ln–Ln distance, the steric overcrowding of the central CH$_2$—CH$_2$ units is extreme. Thus, the ligand to lanthanoid ratio changes to 3:2, which is explained best with a simplified structure like as in Fig. 2b.

In accordance, the linewidth of the ^{31}P NMR is increased strongly because of a decrease in the distance P=O···Ln, while the CH$_2$-carbon signal vanishes because the CH$_2$ groups are much closer to the paramagnetic centers.

Of course, (cyclic)polymer or network structures with multiples of this basic building block, like in the X-ray structure (see below), as well as dynamic structures can explain the spectroscopic data as long as they reflect the symmetry in the spectra with respect to the NMR timescale, but considering the observation that no "endgroups" are detected.

With the purpose to receive an unequivocal structural assignment in the case of tetraethyl ethylenediphosphonate complexes, where the coordinating chelate becomes bigger, a single crystal X-ray structure determination was completed for the complex **3a**. The crystal was obtained from isopropanol solution. All relevant parameters are described in Table 3.

The X-ray diffraction of **3a** confirmed the formula L$_2$La(NO$_3$)$_3$, determined from the elemental analysis data. The asymmetric unit of complex **3a** consists of half a molecule C$_{20}$H$_{48}$LaN$_3$O$_{21}$P$_4$ with La1, N20, and O203 on the crystallographic twofold axis (Fig. 3).

The crystal structure consists of a polymer network with bridged bidentate phosphonate ligands with crystallographic inversion centers between C11 and C11b, respectively, C21 and C21f (Fig. 4).

The lanthanum atom in complex **3a** is surrounded by 10 oxygen atoms, 6 of them are from the three bidentate nitrate ions (O101, O102, O101a, O102a, O201, and O201a) and 4 are from the four phosphonate ligands (O10, O10a, O20, and O20a). The bonds La—OP are in the range 2.4602(11) and

TABLE 3 Crystal Data and Details of the Structure Determination **3a**

|	Crystal Data		
Formula			C$_{20}$H$_{48}$LaN$_3$O$_{21}$P$_4$
Formula weight			929.40
Crystal system			Monoclinic
Space group		C2/c	(no. 15)
a, b, c (Å)	15.1415(4)	14.9749(4)	18.3887(5)
β (°)			114.129(1)
V (Å^3)			3805.2 (2)
Z			4
D (calc) (g/cm^3)			1.622
μ(Mo Kα) (mm^{-1})			1.371
F(000)			1896
Crystal size (mm)			0.40 × 0.40 × 0.30
	Data Collection		
Temperature (K)			153
Radiation (Å)			Mo Kα λ = 0.71073
$\theta_{min} - \theta_{max}$ (°)			2.4, 32.5
hkl Index-range			−22: 19; −18: 22; −27: 27
Tot., Uniq. Data, R (int)			27372, 6823, 0.023
Observed data [$I > 2.0\sigma(I)$]			6586
	Refinement		
N_{ref}, N_{par}			6823, 251
R, $wR2$, S			0.023, 0.058, 1.08
$w = 1/[s^2(F_0^2) + (0.0318P)^2 + 2.6978P]$, where $P = (F_0^2 + 2F_c^2)/3$			
Maximum and average shift/error			0.00, 0.00
Minimum and maximum Resd. Dens. (e/Å^3)			−0.64, 1.19
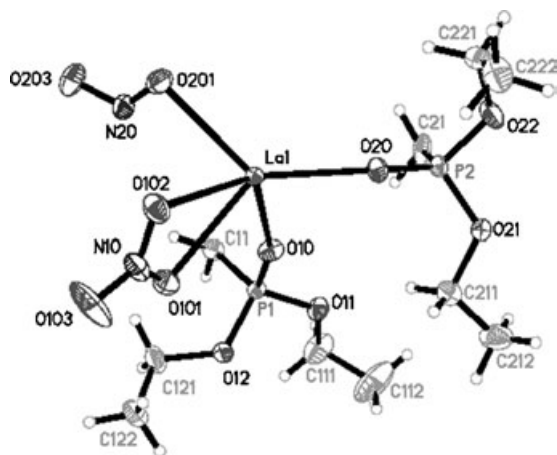
FIGURE 3   Asymmetric unit of complex **3a**.

2.4952(10) Å. These values show that the strength of coordination of the lanthanum ion by phosphoryl groups in **3a** is comparable, and to some extent bigger than those by phosphonamido ligand $(EtO)_2P(O)CH_2CON(CH_3)_2$ **6** [15]. (Bond distances La—OP in **6** are 2.492(3) and 2.500(4) Å.)

In both cases, P=O bonds are lengthened because of coordination: in **3a**, P1—O10 1.4771(11), P2—O20 1.4784(10); in **6** 1.478(4) and 1.485(4) Å.

The La—ONO bond distances range from 2.6239(11) to 2.7296(3) Å and are similar to distances found in a number of lanthanide bidentate nitrate complexes [15,17].

In our previous work, we showed that in the complexes of the diethyl ester of 2-dimethylamino-2-oxoethylphosphonic acid with $La(NO_3)_3$ **6** [15], as well as of the tetraethyl ester of methylenediphosphonate $[(EtO)_2PO]_2CH_2$ with MoO_2Cl_2 [14], the bidentate phosphonate ligands participate in six-membered chelate rings.

The present study shows that when the coordinating chelate becomes bigger (in **3a** seven members) the complexation is realized by linear coordination of the phosphonate ligands.

Complexes of the Tetraisopropyl Ester of Ethylene-diphosphonic Acid (L′) with Lanthanide Nitrates [1]

The coordination of the tetraisopropyl ester of ethylenediphosphonic acid **4** (**L′**) with lanthanide nitrates **1a–d** was studied using almost the same conditions described above for the preparation of complexes **3** (30–60 min stirring in ethanol at room temperature) and a ratio ligand/lanthanide 2:1 or 3:1, comparable with previous procedures [1]. Only in
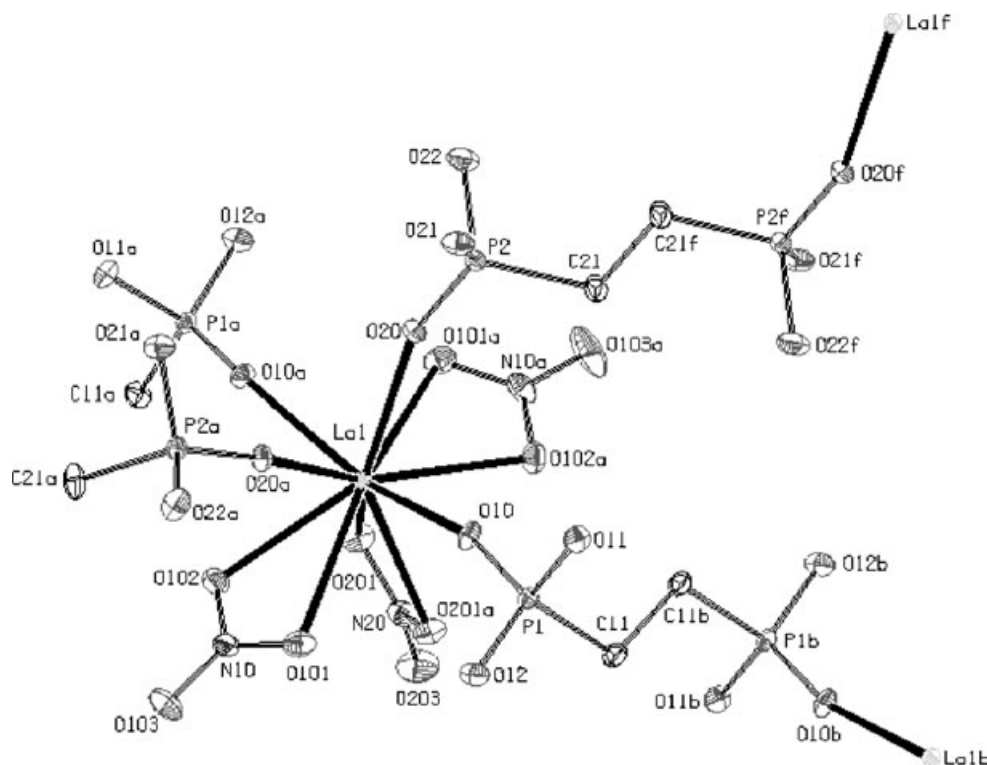

FIGURE 4   Polymeric network of complex **3a** (without ethyl groups).

the experiment with $La(NO_3)_3 \cdot 6H_2O$ (**1a**) for 60 min and a ratio 3:1 no precipitate was formed. The solvent was evaporated and the residue was dispersed in ether/hexane 1:1. The isolated crystalline product **5a′** has a mp of 89–92°, and the elemental analysis showed a ratio 2:1. Oppositely, when the reaction is reproduced with a standing time of the mixture for more than 32 h at –10°C, precipitate was formed with a ratio ligand/lanthanide of 3:2. This product (**5a**) is not described previously [1]. It was also obtained when the ratio of the starting reagents was 3:2 or when the reaction temperature was 50°C. A small impurity of **5a** was isolated from the crude product **5a′** as well. For the complexes **5b, 5c,** and **5d**, the analysis showed the ratio 3:2, independently of the excess of **4**. The formation of two kinds of complexes with different ligand/lanthanide ratio suggests a preferred structure of the complexes with a 3:2 ratio, while at the same reaction conditions for the complexes of the tetraethylesters **2** the structures with a 2:1 ratio are dominant. Obviously, the bulky isopropyl groups influence the type of coordination remarkably. We were not able to transform either **5a** to **5a′** (and reverse) by simple heating of the sample in the NMR tube. The purity of the complexes **3** and **5** could not be increased by recrystallization probably because of their low stability in the solution when heated.

The IR spectra of complexes **5** in Nujol have some specificity with respect to the complexes **3a–d**. The bands for the P—O—C stretching vibrations in **5** (1000–1030 cm^{-1}, s) are not influenced (in **4** 985 br, s). The P=O group in **5a, 5b, 5c,** and **5d** is characterized by three groups of bands 1174–1180 (s), 1202–1215, and 1220–1240 cm^{-1} (see Table 4), while the starting ligand **4** has absorptions at 1247 cm^{-1} in Nujol and 1244 cm^{-1} in KBr, which is an indication of a complicated mode of coordination of P=O groups in these complexes. In **5a′** only, one strong band at 1215 cm^{-1} for the P=O groups is observed, supporting the above-mentioned observations.

The nitrate group in the complexes **5a–d** in Nujol is characterized by a band at about 1300 cm^{-1} (s) and 1500–1515 cm^{-1} (NO$_2$ antisymmetric stretch) [21]. Only in **5a′**, similarly to the complexes **3a, b**, the band at 1500–1515 cm^{-1} is missing, thus confirming different kinds of coordination of the nitrate group in the studied complexes.

In order to obtain more precise data, the IR spectra of **5a′** and **5a** were recorded between KBr disks. In the IR spectrum of **5a′**, the 1500–1400 cm^{-1} and 1350–1270 cm^{-1} regions are characterized with multiple bands with maxima at 1475, 1459, 1440, cm^{-1} and 1313, 1299 cm^{-1}, respectively. These data are similar with the corresponding ones for the complex

TABLE 4 IR Data in Nujol and KBr (in Some Cases) of **4, 5a′**, and **5a–d**

	P—O—C	P=O	NO$_3^-$
4	985	1247 (s)	
4[a]	997	1244 (s)	
5a′	1000 (br)	1215 (s)	1299
			1314
5a′[a]	997	1174	1299
		1202	1313
		1215	1440
		1233	1459
			1475
5a	1010 (br)	1174 (s)	1284
		1202 (s)	1493
		1215 (m)	1509
		1234 (w)	
5a[a]	1005	1174	1286
		1202	1452
		1215	1469
		1233	1492
			1509
5b	1020 (br)	1180 (s)	1295
		1205 (m)	1500
		1220 (s)	1515 (sh)
		1240 (w)	
5c	1020 (br)	1180 (s)	1303
		1210 (s)	1500
		1220 (s)	1515 (sh)
		1240 (m)	
5d	1010	1180 (s)	1300
	1030	1205	1500
		1220 (s)	
		1235 (w)	

[a]In KBr: (s) strong; (m) medium; (w) weak; (sh) shoulder.

3a, where bidentate-chelating coordination of the nitrate groups is proven by X-ray data.

In the spectrum of **5a**, the pairs of peaks are observed at 1469 and 1452 cm^{-1}, belonging to the $\nu_{N=O}$ stretching vibration of bidentate coordinated nitrate groups. The new observed maxima at 1509 cm^{-1}, 1492 cm^{-1}, and an intensive multiple one at 1286 cm^{-1}, corresponding to $\nu_{NO_2}^{as}$ and $\nu_{NO_2}^{s}$, respectively [22,23], document the presence of a monodentate, through one O-atom, linked nitrate fragment, as well.

On the basis of the above-mentioned IR and X-ray data, the bands in Nujol at 1500–1515 cm^{-1} in **5b–d** and **3c–e** are attributed to the presence of monodentate nitrate groups. This suggestion was confirmed by the IR and X-ray data of lanthanoid complexes of methylenediphosphonates [24]. The work is in progress in this respect.

The differences in the IR spectra are present only in the crystalline form, but disappear in methanol—the spectra of **5a** and **5a′** are identical in solution. The same effect in solution has been observed by Stewart and Siddall [25] for the complexes of Dy, Ho, Er, and

**TABLE 5** ^{13}C-Chemical Shifts and Coupling Constants of the P—CH$_2$ group in **4** and **5a–d**

	P(A)-13C(X)-C-P(A')			
	δ (ppm)	J(AX) (Hz)	J(A'X) (Hz)	J(AA')(Hz)
4	20.9(9)	147.0(1)	−6.6(9)	81.7(3)
5a'	20.1(8)	147.0(3)	−5.6(0)	53.6(8)
5a	20.1(4)	152.2(3)	−10.9(8)	42.3(9)
5b	23.5(5)	146.8(9)	−5.8(2)	44.5(6)
5c	20.6(0)	146.9(7)	−5.3(7)	44.4(7)
5d	19.5(1)	146.1(3)	(−5.00)	Not observed

The accuracy is given with respect to the calculation, not to the measurement.

Yb nitrates with tetraisopropyl methylenediphosphonate. However, this observation only holds for the IR spectra, while in the NMR spectra differences are observed (see below). Obviously, the resolving power of IR spectroscopy is not good enough to detect these small changes.

A fast indication for the complexation by the change in the J(AA') coupling (Table 5) is available from the inspection of the DEPT135 spectra [26], optimized for $J_{CH} = 145$ Hz.

For this type of spectra, the lines in the multiplet behave like "CH-couplings" and therefore they are also "multiplicity selected" according to the value of the "coupling constant." In **4**, the distances between the inner and the outer lines represent 140 and 225 Hz, respectively. In this case (Fig. 5), the two outer lines and the two inner lines are 180° out of phase, indicating a J(AA') ∼ 80 Hz. In **5b**, the distances are 140 and 176 Hz, the latter value is close enough to 140 to yield a similar phase result with slight distortions.
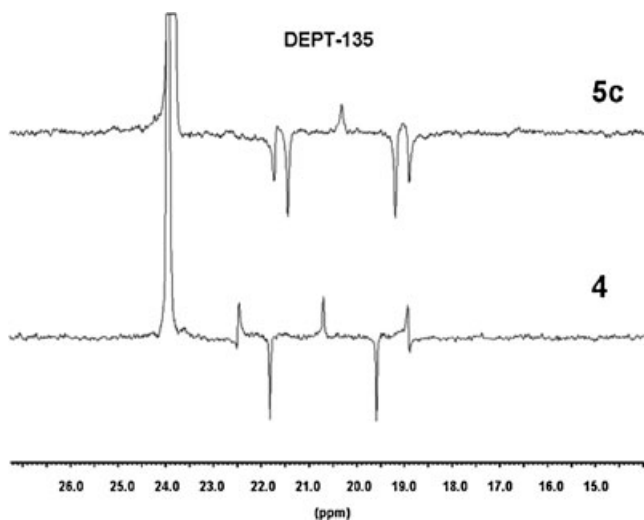
FIGURE 5 ^{13}C-DEPT-135 spectra of the PCH$_2$-signal in **4** and **5c**.

Now, both pairs of lines are in the same direction, representing a J(AA') of ∼45 Hz. Thus, a simple visual inspection of the DEPT spectrum yields a direct evidence for complexation.

Another valuable indication is found in the ^{1}H-NMR spectra of the isopropyl compounds. In the free ligand **4**, only a doublet is observed for the isopropyl-methyl group signal, while in the complexes two doublets are observed. Obviously, determined by stereochemical conflicts, the prochirality of the isopropyl group comes into account and delivers an additional argument for the complexation. However, this splitting is not observed in **5a'** which leads, together with the data in Table 5, to an assumption that in this compound another type of complexation is established, which maybe similar to the polymeric framework like in **3a**.

CONCLUSION

Extending the central chain length from usual phosphonates to ethylene diphosphonates changes the type of complexation for lanthanide nitrates from chelating ring structures to a linear, multiple phosphonate ligand binding coordination, up to a networked situation in the crystalline state. It must be expected that this strong change in the structural features has remarkable consequences for the application of these types of compounds in extraction and drug research.

EXPERIMENTAL SECTION

The phosphonate ligands **2** and **4** were prepared and purified according to the literature [27,28]. Anhydrous ethanol and commercial lanthanide nitrates were used. Analytical data were obtained from the Microanalytical Laboratory of the Department of Chemistry, University of Sofia. The ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a VARIAN Gemini 2000 BB or a BRUKER WM-250 in either 5 or 10 mm tubes at room temperature. The ^{1}H NMR spectra were referenced to internal TMS, ^{13}C NMR spectra relative to the corresponding solvent signals, and ^{31}P NMR spectra to external 85% aq. H$_3$PO$_4$. The ^{13}C multiplicity was determined via APT spectra [29]. The integral values are given for one ligand of the molecule. The IR spectra were registered on Specord-71 IR and Perkin-Elmer 1720 FTIR spectrometers.

Synthesis of the complexes **3a–e** and **5a–d**

General Procedure.   A solution of lanthanide nitrate **1** (1 mmol) in 1.5–2.5 mL of ethanol was added

to 2–3 mmol of diphosphonate ester **2** (respectively, **4**). The reaction mixture was stirred for 30–60 min at room temperature, and the precipitate thus formed was filtered off, washed with ethanol/ether 1:3 and then with ether, and dried in vacuum. In some cases, the products were washed once more by stirring with the above mixture of solvents (ethanol/ether 1:3).

Tetraethyl Ethylenediphosphonate Lanthanum (III) Nitrate L$_2$La(NO$_3$)$_3$ **3a.** From 0.604 g (2 mmol) **2** and 0.433 g (1 mmol) of La(NO$_3$)$_3$·6H$_2$O **1a** in 2.5 mL ethanol 0.780 g (84%) of **3a** was obtained with mp 142.5–144°C. The white crystalline product is soluble in methanol, ethanol, isopropanol, and chloroform and less soluble in acetone. Found: C, 26.11; H, 5.15; N, 4.82. C$_{20}$H$_{48}$N$_3$O$_{21}$P$_4$La (929.403) requires C, 25.85; H, 5.21; N, 4.52%. IR: ν_{max} (Nujol) (cm^{-1}): 1021 and 1035 (s) (P—O—C); 1189, 1208 (s), 1220(s) (P=O), 1325 (s) (nitrate band). IR (KBr) ν_{max} (cm^{-1}): 1021 and 1035 (P—O—C), 1208 and 1220 (P=O), 1332 and 1324 (ν_{NO}), 1446–1484 ($\nu_{N=O}$) in bidentate-coordinated NO$_3$ group. ^{1}H-NMR δ^1H (ppm, CD$_3$OD): 1.35 [12H, t, *J*(HH) 7.06 Hz, OCH$_2$CH$_3$], 2.09 [4H, m, P-CH$_2$], 4.13–4.20 [8H, m, OCH$_2$CH$_3$]; ^{13}C{^{1}H}-NMR δ^{13}C (ppm, CD$_3$OD): 16.62 [t, *J*(C1P) 3.01 Hz, OCH$_2$CH$_3$], 18.69 [CH$_2$, center of the X-part of AA′X system], 64.22 [t, *J*(C2P) 3.05 Hz, OCH$_2$CH$_3$].
^{31}P{^{1}H} NMR δ^{31}P(CD$_3$OD): 31.14 ppm.

Tetraethyl Ethylenediphosphonate Cerium (III) Nitrate L$_2$Ce(NO$_3$)$_3$ **3b.** Using the general procedure from 0.604 g (2 mmol) of **2** and 0.434 g (1 mmol) Ce(NO$_3$)$_3$·6H$_2$O (**1b**) in 2.5 mL ethanol, 0.650 g (70%) white crystalline **3b** was obtained with mp 132–134°C. The product is soluble in methanol and chloroform and less soluble in ethanol, isopropanol, and acetone. Found: C, 25.76; H, 4.89; N, 4.84. C$_{20}$H$_{48}$N$_3$O$_{21}$P$_4$Ce (930.614) requires C, 25.81; H, 5.20; N, 4.52%. IR: ν_{max}(Nujol) (cm^{-1}): 1010–1030 (s) (P—O—C); 1195, 1210, and 1225 (s) (P=O), 1330 (s) (nitrate band). ^{1}H-NMR δ^1H (ppm, CD$_3$OD): 1.34 [12H, t, *J*(HH) 7.06 Hz, OCH$_2$CH$_3$], 3.10 [4H, m, broad, P-CH$_2$], 4.19–4.27 [8H, m, OCH$_2$CH$_3$]; ^{13}C{^{1}H}-NMR δ^{13}C (ppm, CD$_3$OD): 16.70 [t, *J*(C1P) 2.67 Hz, OCH$_2$CH$_3$], 20.77 [CH$_2$, center of the X-part of AA′X system], 64.67 [*J*(C2P) 2.86 Hz, OCH$_2$CH$_3$].
^{31}P{^{1}H} NMR δ^{31}P(CD$_3$OD): 40.12 ppm (broad).

Tetraethyl Ethylenediphosphonate Samarium (III) Nitrate L$_2$Sm(NO$_3$)$_3$ **3c.** 0.665 g of **2** and 0.444 g (1 mmol) Sm(NO$_3$)$_3$·6H$_2$O (**1c**) in 1.5 mL ethanol were reacted to give 0.590 g (60%) of **3c** (white crystalline product) with mp 154–155°C. It is soluble in methanol, acetone, and chloroform and less soluble in ethanol and isopropanol. Found: C, 23.95; H, 4.60; N, 4.95. C$_{20}$H$_{48}$N$_3$O$_{21}$P$_4$Sm.2H$_2$O (976.888) requires C, 24.59; H, 5.37; N, 4.30%. IR: ν_{max} (Nujol)/ cm^{-1}: 1017 (br, s) (P—O—C); 1185 and 1222(s) (P=O) 1299, 1514 (s) (nitrate band) ^{1}H-NMR δ^1H (ppm, CD$_3$OD): 1.34 [12H, t, *J*(HH) 7.01 Hz, OCHCH$_3$], 2.21 [4H, m, broad, P-CH$_2$], 4.15–4.19 [8H, m, OCH$_2$CH$_3$]. ^{13}C{^{1}H}-NMR δ^{13}C (ppm, CD$_3$OD): 16.61 [t, *J*(C1P) 2.86 Hz, OCH$_2$CH$_3$], 18.97 [CH$_2$, center of the X part of AA′X system], 64.55 [broad, OCH$_2$CH$_3$].
^{31}P{^{1}H} NMR δ^{31}P(CD$_3$OD): 31.18 ppm.

Tetraethyl Ethylenediphosphonate Europium(III) Nitrate L$_2$Eu(NO$_3$)$_3$ **3d.** From 0.604 g (2 mmol) of **2** and 0. 428 g (1 mmol) Eu(NO$_3$)$_3$·5H$_2$O (**1d**) in 2.5 mL ethanol, using the general procedure 0.64 g (68%) of **3d** was isolated with mp 154–156°C. The product is soluble in methanol and ethanol and less soluble in isopropanol and acetone. Found: C, 25.05; H, 4.75; N, 4.96. C$_{20}$H$_{48}$N$_3$O$_{21}$P$_4$Eu (942.462) requires C, 25.49; H, 5.13; N, 4.46%. IR: ν_{max} (Nujol)/ (cm^{-1}):1010 and 1020 (s) (P—O—C); 1180 (s) and 1210 (m)(P=O), 1300 (s), 1505 (nitrate band). ^{1}H-NMR δ^1H (ppm, CD$_3$OD): 1.33 [12H, t, *J*(HH) 7.06 Hz, OCH$_2$CH$_3$], 1.55–1.65 [4H, m, broad, P-CH$_2$], 4.05–4.09 [8H, m, OCH$_2$CH$_3$]; ^{13}C{^{1}H}-NMR δ^{13}C (ppm, CD$_3$OD): 16.46 [t, *J*(C1P) 2.86 Hz, OCH$_2$CH$_3$], 18.65 [CH$_2$, center of the X part of AA′X system, ^{1}*J*(CP) 140.74] [30], 64.19 [*J*(C2P) 2.86 Hz, OCH$_2$CH$_3$].
^{31}P{^{1}H} NMR δ^{31}P(CD$_3$OD): not observed.

Tetraethyl Ethylenediphosphonate Erbium(III) Nitrate L$_3$[Er(NO$_3$)$_3$]$_2$ **3e.** 0.604 g (2 mmol) of **2** and 0.443 g (1 mmol) Er(NO$_3$)$_3$·5H$_2$O (**1e**) in 2.5 mL ethanol react to give 0.65 g (81%) **3e** with mp 152–152°C. The product (pale rose crystals) is soluble in methanol, ethanol, and chloroform and less soluble in isopropanol and acetone. Found: C, 22.53; H, 4.86; N, 4.99. C$_{30}$H$_{72}$N$_6$O$_{36}$P$_6$Er$_2$ (1613.272) requires C, 22.33; H, 4.50; N, 5.21%. IR: ν_{max} (Nujol)/ (cm^{-1}): 1010 and 1030 (s) (P—O—C); 1190, 1210, and 1230 (s) (P=O), 1310 (s), 1500, 1515 (s) (nitrate bands). ^{1}H-NMR δ^1H (ppm, CD$_3$OD): 1.29 [12H, broad, OCH$_2$CH$_3$], 4.3–4.5 [8H, m, very broad, OCH$_2$CH$_3$]; ^{13}C{^{1}H}-NMR δ^{13}C (ppm, CD$_3$OD): 16.24 [OCH$_2$CH$_3$, broad], 62.60 [OCH$_2$CH$_3$, broad]. Central CH$_2$ not observed.
^{31}P{^{1}H} NMR δ^{31}P(CD$_3$OD): not observed.

Tetraethyl Ethylenediphosnate **2.** IR: ν_{max} (Nujol)/ (cm^{-1}): 1035 and 1055 (P—O—C), 1260 (P=O) IR: ν_{max} (KBr)/ (cm^{-1}): 1028 and 1048 (P—O—C), 1246 (P=O).

Tetraisopropyl Ethylenediphosphonate Lanthanum(III) Nitrate $L'_2.La(NO_3)_3$ **5a′** *[1].* A solution of 0.433 g (1 mmol) $La(NO_3)_3 6H_2O$ (**1a**) in 2.5 mL ethanol was added to 1.09 g (3 mmol) tetraisopropyl ethylene diphosphonate (**4**). The mixture is stirred for 60 min (no precipitate was observed), and the solvent was evaporated in vacuum at temperature of the bath 30–40°C. The crude product was dissolved in anhydrous ether (3 mL), and after addition of 3 mL of hexane the precipitate thus formed was filtered off (0.44 g, mp 88–92°C, **5a′** and small impurity with mp 115–140°C). From the filtrate was isolated 0.250 g of **5a′** as well, with mp 88–92°C. The white crystalline product with mp 89–92°C is soluble in most solvents and less soluble in hexane.

After treating of the crude **5a′** with ethanol/ether 1:5 a small quantity of a product with mp 185–195° was isolated. Its mp, IR, and elemental analyses are equal to those of a complex **5a**.

Found: C, 33.07; H, 6.55; N, 4.00. $C_{28}H_{64}N_3O_{21}P_4La$ (1041.616) requires C, 32.29 H, 6.19; N, 4.03%. IR: ν_{max} (Nujol)/ (cm^{-1}): 1000 (br, s) (P—O—C); 1215 (s)(P=O), 1299 and 1314 (s), (nitrate band). IR (KBr): 997(P—O—C), 1174, 1202, 1215, and 1233 (P=O), 1299 and 1313 (ν_{NO}), 1440, 1459, and 1475 ($\nu_{N=O}$). ^{1}H-NMR δ^1H (ppm, CD$_3$OD): 1.34 [24H, d, J(HH) 6.17 Hz, OCHC$\underline{H}_3$], 1.97 [4H, m, P-CH$_2$], 4.67–4.81 [4H, m, OC$\underline{H}$]; ^{13}C{^{1}H}-NMR δ^{13}C (ppm, CD$_3$OD): 20.18 [m, $\underline{C}$H$_2$, center of the X part in AA′X system], 24.13–24.21 [m, J(CP) 2.49 Hz, OCHC$\underline{H}_3$], 73.42 [t, J(C2P) 3.46 Hz, OC$\underline{H}$].
^{31}P{^{1}H} NMR δ^{31}P(CD$_3$OD): 28.85 ppm.

Tetraisopropyl Ethylenediphosphonate Lanthanum(III) Nitrate $L'_3.[La(NO_3)_3]_2$ **5a**. The reaction mixture of 1 mmol **1a** and 2 mmol **4** in 1.5 mL ethanol was stirred for 30 min and then left 32 h at −10°C. The precipitate formed was filtered off and washed with ethanol/ether (5:1) and then with ether and dried in vacuum. The white crystalline product **5a** (0.370 g, 43%) has mp 198–199.5°C. Found: C, 29.80; H, 6.24; N, 4.53. $C_{42}H_{96}N_6O_{36}P_6La_2$ (1724.884) requires C, 29.25; H, 5.61; N, 4.87%. IR: ν_{max} (Nujol)/ (cm^{-1}): 1010 (br, s) (P—O—C); 1174, 1202 (s), 1215 (m) and 1234 (w) (P=O); 1284, 1493, 1509 (s) (nitrate bands). IR (KBr) 1005 (P—O—C), 1174, 1202, 1215, and 1233 (P=O), 1286 (m, $\nu^{as}_{NO_2}$ in monodentate nitrate group), 1452 and 1469 ($\nu_{N=O}$ in bidentate nitrate group), 1492 and 1509 ($\nu^{as}_{NO_2}$ in monodentate nitrate group. ^{1}H-NMR δ^1H (ppm, CD$_3$OD): 1.32 [12H, d, J(HH) 1.10 Hz, OCHC$\underline{H}_3$], 1.36 [12 H, d, J(HH) 1.28 Hz, OCHC$\underline{H}_3$], 2.01 [4H, m, P-CH$_2$], 4.67–4.88 [4H, m, OC$\underline{H}$]. ^{13}C{^{1}H}-NMR δ^{13}C (ppm, CD$_3$OD): 20.14 [m, $\underline{C}$H$_2$, center of the X part in AA′X system], 24.13,

24.16, and 24.21 [J(CP) 2.49 Hz, OCHC$\underline{H}_3$] 73.48 [t, J(C2P) 3.43 Hz, OC$\underline{H}$].
^{31}P{^{1}H} NMR δ^{31}P(CD$_3$OD): 28.70 ppm.

Tetraisopropyl Ethylenediphosphonate Cerium (III) Nitrate $L'_3.[Ce(NO_3)_3]_2$ **5b** *[1].* 0.717 g (2 mmol) of **4** and 0.434 g (1 mmol) Ce(NO$_3$)$_3 \cdot 6H_2O$ (**1b**) in 1.5 mL ethanol react to give 0.510 g (59%) of **5b**. The white crystalline product with mp 202–203°C is soluble in methanol, ethanol, acetone, chloroform and less soluble in isopropanol. Found: C, 29.71; H, 5.92; N, 4.68. $C_{42}H_{96}N_6O_{36}P_6Ce_2$ (1727.305) requires C, 29.20; H, 5.60; N, 4.87%. IR: ν_{max} (Nujol)/ (cm^{-1}) 1020 (br, s) (P—O—C); 1180 (s), 1205 (m), 1220 (s) 1240 (w) (P=O); 1295, 1500 (s), 1515 (sh) (nitrate bands). ^{1}H-NMR δ^1H (ppm, CD$_3$OD): 1.28 [12H, d, J(HH) 3.21 Hz, OCHC$\underline{H}_3$], 1.30 [12H, d, J(HH) 2.99 Hz, OCHC$\underline{H}_3$], 4.17 [4H, s (br), P-C$\underline{H}_2$], 4.74–4.77 [4H, m, OC$\underline{H}$]. ^{13}C{^{1}H}-NMR δ^{13}C (ppm, CD$_3$OD): 23.55 [m, $\underline{C}$H$_2$, center of the X part in AA′X system], 24.28 [s, OCHC$\underline{H}_3$], 74.15 [s, OC$\underline{H}$].
^{31}P{^{1}H} NMR δ^{31}P(CD$_3$OD): 44.72 ppm.

Tetraisopropyl Ethylenediphosphonate Samarium(III) Nitrate $L'_3.[Sm(NO_3)_3]_2$ **5c** *[1].* From 0.717 g (2 mmol) of **4** and 0.444 g Sm (NO$_3$)$_3 \cdot 6H_2O$ (**1c**) in 1.5 mL ethanol using the general procedure 0.75 g (86%) of **5c** (white crystals) was isolated with mp 204–205°C, soluble in methanol, ethanol, acetone and less soluble in isopropanol. Found: C, 28.27; H, 5.76; N, 4.61. $C_{42}H_{96}N_6O_{36}P_6Sm_2$ (1747.793) requires C, 28.86; H, 5.54; N, 4.81%. IR: ν_{max} (Nujol)/ (cm^{-1}) 1020 (s, br) (P—O—C); 1180, 1210, 1220 (s), 1240 (m) (P=O); 1303, 1500(s), 1515 (sh) (nitrate bands). ^{1}H-NMR δ^1H (ppm, CD$_3$OD): 1.33 [12H, d, J(HH) 4.2 Hz, OCHC$\underline{H}_3$], 1.36 [12H, d, J(HH) 4.4 Hz, OCHC$\underline{H}_3$], 2.40 [4H, m, P-C$\underline{H}_2$], 4.71–4.82 [4H, m, OC$\underline{H}$]. ^{13}C{^{1}H}-NMR δ^{13}C (ppm, CD$_3$OD): 20.60 [m, CH$_2$, center of the X part in AA′X system], 24.13–24.20 [OCHCH$_3$], 74.01 [t, J(C2P) 3.06 Hz, OCH].
^{31}P{^{1}H} NMR δ^{31}P(CD$_3$OD): 28.46 ppm.

Tetraisopropyl Ethylenediphosphonate Europium (III) Nitrate $L'_3[Eu(NO_3)_3]_2$ **5d**. From 0.402 g (1.12 mmol) of **4** and 0.240 g (0.56 mmol) Eu(NO$_3$)$_3 \cdot 5H_2O$ (**1d**) in 0.75 mL ethanol using the general procedure 0.390 g (78%) of **5d** was obtained (white crystals with mp 202–205°C). The product is soluble in methanol, chloroform, and less soluble in ethanol, isopropanol, and acetone. Found: C, 27.86; H, 5.66; N, 5.03. $C_{42}H_{96}N_6O_{36}P_6Eu_2 \cdot 2H_2O$ (1787.031) requires C, 28.23; H, 5.64 N, 4.70%. IR: ν_{max} (Nujol)/ (cm^{-1}): 1180,1205, 1220 (s), 1235 (w) (P=O); 1300, 1500 (s) (nitrate bands). ^{1}H-NMR δ^1H (ppm, CD$_3$OD):

1.31 [12H, d, J(HH) 6.23 Hz, OCHC$\underline{H}_3$], 1.39 [12H, d, J(HH) 6.04 Hz, OCHC$\underline{H}_3$], 0.58 [4H, m, P-C$\underline{H}_2$], 4.55–4.64 [4H, m, OC$\underline{H}$]. ^{13}C{^{1}H}-NMR δ^{13}C (ppm, CD$_3$OD): 19.51 [m, $\underline{C}$H$_2$, center of the X part in AA′X system], 23.89 [s, OCH$\underline{C}$H$_3$], 73.59 [d, J(C2P) 6.59 Hz, O$\underline{C}$H].

^{31}P{^{1}H} NMR δ^{31}P(CD$_3$OD): 44.72 ppm.

Tetraisopropyl Ethylenediphosphonate **4**. IR (Nujol) ν_{max} (cm^{-1}): 985 (s, br) (P—O—C); 1247 b(P—O). IR (KBr) ν_{max} (cm^{-1}): 997 (s, br) (P—O—C); 1244 (P=O).

X-RAY CRYSTALLOGRAPHIC STUDY:

Suitable crystals were obtained by recrystallization from i-PrOH. The data were collected on a Bruker APEX CCD diffractometer using MoKα radiation from a prismatic crystal with size 0.40 × 0.40 × 0.30 mm at 153 K. 27372 reflections were measured. After averaging of the symmetrically equivalent reflections, 6823 unique reflections were obtained; 6586 with $I > 2\sigma(I)$. Direct methods SHELXS-97 [31] and successive interpretation of difference Fourier maps, followed by least-squares refinement SHELXL-97 [32] solved the structures. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions. The final R-values are $R_1 = 0.023$ for all and 0.022 for the significant reflections. Further details of the data collections are summarized in Table 3.

CCDC-226551 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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