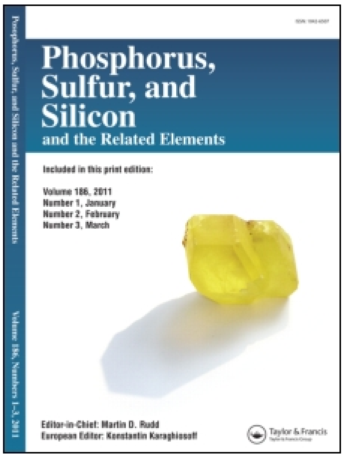

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Synthesis and Structure of Complexes of the Diethyl Ester of 2-Dimethylamino-2-oxoethylphosphonic Acid with Lanthanide Nitrates

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SYNTHESIS AND STRUCTURE OF COMPLEXES OF THE DIETHYL ESTER OF 2-DIMETHYLAMINO-2-OXOETHYLPHOSPHONIC ACID WITH LANTHANIDE NITRATES

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*The lanthanide complexes $LnL_2(NO_3)_3$ **(3a–g)** are obtained where Ln is La, Sm, Yb, Er, Ce, Eu, Gd, and L is the diethyl ester of 2-dimethylamino-2-oxoethylphosphonic acid $[(C_2H_5O)_2P(O)CH_2CON(CH_3)_2]$ **1**. They are characterized by elemental analysis, i.r. and NMR spectroscopy. The crystal structure of **3a** is determined by single crystal X-ray diffraction. The complex is found to crystallize in the triclinic space group $\bar{P}1$ with $a = 8.4220(17)$ Å, $b = 11.123(2)$ Å, $c = 17.560(4)$ Å, $\alpha = 87.20(3)^\circ$, $\beta = 82.27(3)^\circ$, $\gamma = 76.89(3)^\circ$, $V = 1587.3(5)$ Å^3, $Z = 2, \rho_{calcd} = 1.614$ mg/m^3, $R = 0.047, R_w = 0.107, S = 1.034$ for 5762 reflections with $I > 2\sigma(I)$. The structure contains monomeric units of the complex with the lanthanum atom coordinated by 10 oxygen atoms, six of them from the three bidentate nitrate ions and four from the two phosphonate ligands. The coordination is realized by both phosphoryl and amide-carbonyl oxygen atoms.*

*The stereochemistry of the starting ligand **1** is investigated by NMR spectroscopy.*

Keywords: Complexes; diethyl ester of 2-dimethylamino-2-oxoethylphosphonic acid; lanthanide nitrates; NMR (^{1}H,^{13}C,^{31}P); x-ray diffraction

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INTRODUCTION

The application of organophosphorus compounds as ligands in coordination chemistry has gained considerable importance due to their ability for various modes of coordination[1–3] and their use for extraction and partitioning of different metals. In our previous works we described the synthesis and structures of complexes of transition, nontransition and lanthanide elements with 2-oxo-phosphonates[4–6] and phosphine oxides,[7,8] where the coordinating centers were the oxygen atoms of the P=O and aldehyde groups. In extension of this work it was interesting to study the role of the amide oxygen and the structure of the lanthanide complexes of carbamoylmethylphosphonates. The literature data showed that their coordinating ability and the way of coordination depends strongly on the metal salt, as well as on the substituents of the phosphorus and amide nitrogen atoms.[9–13] For example, in the complex of DiPDECMP (diisopropyl N,N-diethylcarbamoyl-methylphosphonate) with Sm(III) nitrate the metal ion is bonded to both carbonyl and phosphoryl oxygen atoms (coordination number 10), while in the corresponding erbium complex the metal ion is not bonded to the carbonyl oxygen atom of the amide group (coordinating number 9).[11] We report here the synthesis and characterization of the complexes of the diethyl ester of 2-dimethylamino-2-oxoethylphosphonic acid **1** (L) with lanthanide nitrates **2**, as well as a single crystal x-ray diffraction of the lanthanum complex **3a**.

RESULTS AND DISCUSSION

At first the stereochemistry of the starting phosphonoacetamide **1** (Figure 1) was investigated by NMR spectroscopy.

Two signals (at 3.00 and 2.78 ppm, see Experimental section) were observed in the ^{1}H-NMR spectrum in DMSO for the N—CH$_3$ protons at C5 and C6 obviously due to a hindered rotation around the N—CO bond. The upfield signal shows a coupling to the phosphorus, which is also resolved in some of the complex spectra (see Experimental section). To exclude the existence of two different molecules a temperature

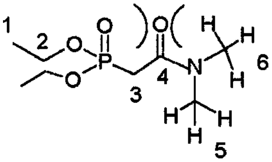


FIGURE 1 Structure of the ligand L (**1**).

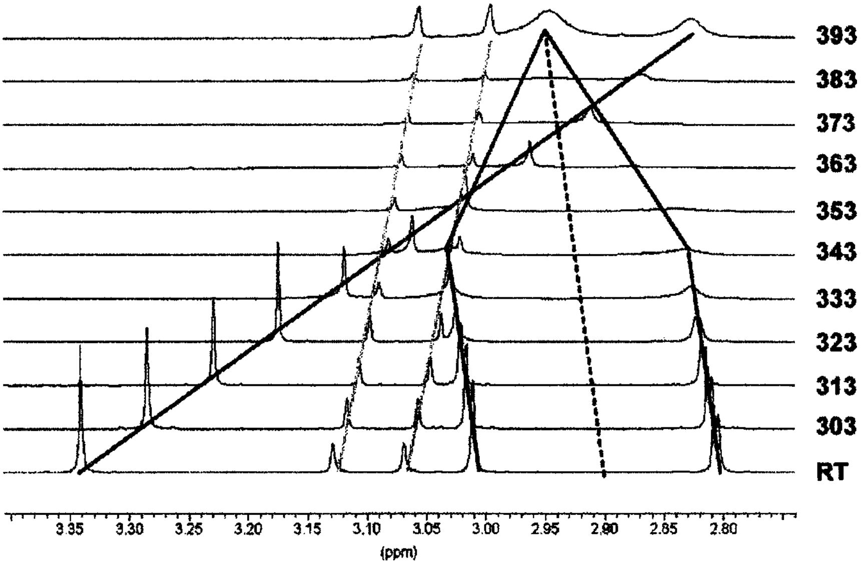
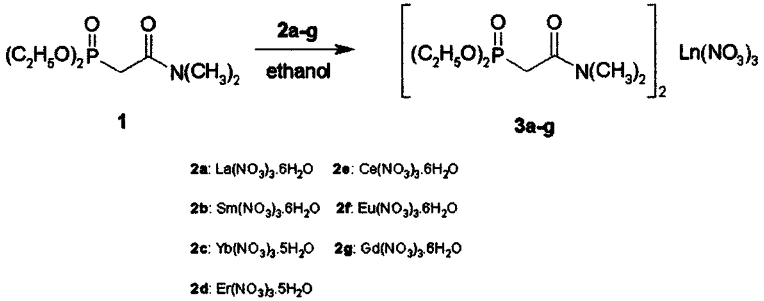


FIGURE 2 Temperature dependent ^{1}H-NMR measurement of the ligand L (**1**).

dependent measurement was carried out in the interval T (303–393 K). This dependence is shown on Figure 2, where the signal with the stronger upfield shift from lower to higher temperature is due to residual water in the solvent. The doublet at 3.09 ppm, due to the CH_2-group at C3 [J(PH) = 21.6 Hz], shifts upfield while the methyl groups shift parallel downfield until coalescence.

It is obvious that all signals are strongly temperature dependent. Concerning the methyl signals, at first the small long range coupling to the phosphorus breaks down. Around T = 333 K there is an overlap and crossing at ~3.05 ppm with the signal of H3. The methyl signals are broadened at this temperature and start to coalescence which is finished at around T 393 K, exactly in the center of the signal. The dotted line (....) shows the concerted behavior of the signals. Thus it is proven that the spectrum is from one compound. This conclusion is confirmed by the ^{31}P{H}-NMR spectrum of **1**, which contains only one signal at 23.19 ppm. The assignment of H5 versus H6 (Figure 1) was made on the basis of a long-range W mechanism, which is the reason of a long-range coupling: in **1** ^5J(H6P) = 1.30 Hz in DMSO, 1.46 Hz in acetone; in **3a** 1.22 Hz in acetone (see Experimental). The upfield shift of H6 versus H5 is consistent with the Figure 1, because the protons come close to the anisotropy cone of the C=O group. The correlation of H5,6 to C5,6 was proven via a 2D-HETCOR-spectrum. The lanthanide complexes **3a–g** were obtained from the ligand L (**1**) and the corresponding lanthanide nitrates **2a–g** in ethanol at room temperature. The experiments were carried out in a ratio ligand/nitrate 2:1 or 3:1. The elemental analysis showed in both cases a molecular formula $LnL_2(NO_3)_3$, where Ln is La, Sm, Yb, Er, Ce, Eu, Gd, and L is $(C_2H_5O)_2P(O)CH_2CON(CH_3)_2$ (see Scheme 1).



SCHEME 1 Synthesis of the complexes $LnL_2(NO_3)_3$ **3a–g**.

The yields of the complexes are higher at the ratio ligand/lanthanide nitrate 3:1. The isolated **3a**, **3b**, **3e**, **3f**, and **3g** are white crystals, **3c** is a colorless oil and **3d** is a rose-colored oil, which crystallized after long staying. They are soluble in water, DMSO, methanol, not well soluble in ethanol, $CHCl_3$, and CH_2Cl_2. The complexes **3a**, **b**, **d–f** are soluble in acetone.

The IR spectra of the complexes in nujol (**3c** as film) contained absorption at 1210–1220 cm^{-1} and 1620–1630 cm^{-1} respectively due to P=O and C=O valence vibrations, thus complexation producing low frequency shifts of 60–70 cm^{-1}, respectively 40–50 cm^{-1} of these bands in respect to the starting **1** (ν_{PO} 1280 cm^{-1}; ν_{CO} 1670 cm^{-1}). The considerable shift of both phosphoryl and amide carbonyl groups indicates bidentate coordination of the lanthanide ion with the oxygen atoms of these groups in the complexes **3**. The characterization of the nitrate groups in nujol is based on the N=O valence frequence ν_1 at about 1300 cm^{-1} (in **2a** at 1310 cm^{-1}, in **3a–g** at 1315–1325 cm^{-1}) which is in accordance with the data for analogous complexes.[10]

The NMR spectra were recorded in DMSO and acetone. In DMSO the signals are slightly shifted upfield in respect to the corresponding signals in the ligand **1**, but the differences are very small (~0.12–0.13 ppm, see Experimental section, **3a**,**b**) and we could expect that there is no really close contact in solution between the lanthanoid ions and the ligand.

In acetone the complexes **3** seems to be stable. The $^{31}P\{H\}$ spectrum of **3a**, **3b**, and **3f** showed singlets at 25.94, 25.90, and −47.50 ppm

TABLE I Crystallographic Data for the Diethyl Ester of 2-Dimethylamino-2-oxoethylphosphonic acid. Lanthanum (III) Nitrate $LaL_2(NO_3)_3$ (**3a**)

Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	8.4220(17)
b, Å	11.123(2)
c, Å	17.560(4)
α, deg	87.20(3)
β, deg	82.27(3)
γ, deg	76.89(3)
V, Å^3	1587.3(5)
Z	2
Crystal color, habit	Colorless block
F(000)	780
M_m	771.35
Crystal size, mm	0.60 × 0.60 × 0.30
ρ_{calcd}	1.614 mg/m^3
Radiation	MoKα($\lambda = 0.71069$ Å)
Temperature, K°	153(2)
Monochromator	Graphite crystal
2θ range	4.5°–55.0°
	h from −2 to 10
	k from −14 to 14
	l from −22 to 22
Scan type	$\bar{\omega}/2\theta$
Reflections collected	10099
Unique reflections	7323
Significant reflections	5762, with $I > 2\sigma(I)$
R, wR, S	0.047, 0.107, 1.034

respectively, which, for **3a** and **3b**, is about 3.5 ppm downfield from the free ligand resonance (22.38 ppm). $^{13}C\{^1H\}$- and ^1H-NMR spectra also showed significant shifts of the C4 resonance (downfield 2.18 ppm for **3a** and 4.02 ppm for **3b**; upfield 22.56 ppm for **3f**), as well as of the CH_2-proton resonance (upfield 2.93 ppm for **3a** ppm and 1.55 ppm for **3b**; downfield 1.49 ppm for **3f**).

The spectral data are consistent with bidentate ligand coordination with lanthanide ions, but they do not provide an unequivocal structure assignment for the complexes. With this purpose, single crystal x-ray structural determination was completed for the lanthanum complex **3a**. All relevant parameters are given in Table I.

The x-ray diffraction of **3a** confirmed the formula $L_2La(NO_3)_3$. The lanthanum atom is surrounded by 10 oxygen atoms, 6 of which are from the 3 bidentate nitrate ions and 4 are from the two phosphonate ligands (Figure 3).

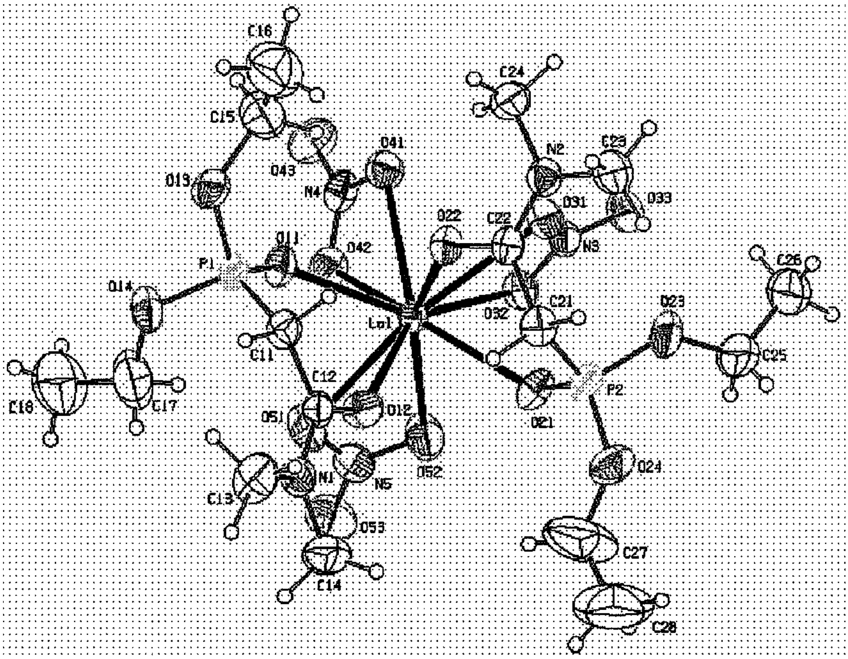


FIGURE 3 X-ray structure of the complex $La[(C_2H_5O)_2P(O)CH_2CON(CH_3)_2]_2(NO_3)_3$ **3a**.

The coordination is realized by both oxygen atoms of phosphoryl and amide-carbonyl groups. This type of coordination is different for the coordination mode of the familiar ligand DiPDECMP with Er(III) nitrate.[11] The bonds La—O are in the range 2.492(3)–2.714(4) Å, where the shown numbers correspond to the distance La—OP and La—ONO_2. The bonds and the angles are not influenced and have typical values, with the exception of P=O and C=O groups, which are lengthened because of the coordination with the lanthanum atom and the values are: P1 O11 1.478(4) Å and P2 O21 1.485(4) Å; C12 O12 1.242(6) Å and C22 O22 1.252(6) Å. The angles O—La—O are in the range 47.46(15)°–75.76 (12)°.

In conclusion, our investigation showed that the dimethylamino group in 2-dimethylamino-2-oxoethylphosphonate increases the coordinating ability of the carbonyl group in comparison with 2-oxoethylphosphonate and phosphine oxide, whose lanthanide complexes are derivatives only of their enolate forms. While the latter could be used to separate lanthanide ions in alkaline medium, the ligand **1** could be applied for extraction in neutral or acidic medium.

EXPERIMENTAL

The ligand **1** was prepared and purified according to the literature.[14] Commercial lanthanide nitrate and anhydrous ethanol was 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 200 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_3PO_4. The ^{13}C multiplicity was determined via APT spectra.[15] The integral values are given for one ligand of the molecule. The spectra of the complexes **3c**, **3d**, **3e**, and **3g** are only measured in DMSO and are close to the ligand spectra (see text). Therefore they are not added in the experimental data. The IR spectra were registered on Specord-71 IR.

Synthesis of the Complexes 3a–g

General Procedure

A solution of lanthanide nitrate **2** (1 mmol) in 6 mL of ethanol was added to diethyl ester of 2-diethylamino-2-oxoethylphosphonic acid **1** (0.446 g, 2 mmol, or 0.670 g, 3 mmol). The reaction mixture was stirred for 1 h at room temperature and after that 10 min at −10°C. The precipitates thus formed were filtered off, washed with hexane (2 × 2 mL), and recrystallized from isopropanol. The obtained, in some cases oily, products were washed with isopropanol and dried in vacuum.

Diethyl Ester of 2-Dimethylamino-2-oxoethylphosphonic Acid

*Lanthanum (III) nitrate $LaL_2(NO_3)_3$ (**3a**).* From **1** (0.446 g, 2 mmol) and $La(NO_3)_3{\cdot}6H_2O$ **2a** (0.433 g, 1 mmol), 0.660 g (86%) raw product with m.p. 148–149°C was obtained. After recrystallization from i-PrOH we obtained white crystals of **3a** (0.484 g, 63%) with m.p. 148.5–149.5°C. Using the same method but from 3 mmol of **1** (0.670 g) and 1 mmol of **2a**, 0.700 g (91%) of a product with m.p. 147–148°C was obtained. After recystallization from i-PrOH 0.595 g (77%) of **3a** were isolated with m.p. 148.5–149.5°C. Found: C, 25.44; H, 4.78; N, 8.63. $C_{16}H_{36}N_5O_{17}P_2La$ (771.34) requires C, 24.91; H, 4.70; N, 9.08%. IR: $\nu_{\max}$ (nujol)/cm^{-1}: 1020 and 1060 (P—O—C), 1210 (P=O), 1620 (C=O). ^{1}H-NMR (DMSO-d$_6$) δ_H: 1.07 (6 H, t, $C\underline{H}_3CH_2O$), 2.67 [3 H, d, *J*(H6P) 1.22 Hz, N—$C\underline{H}_3$], 2.87 (3 H, s, N—$C\underline{H}_3$), 2.96 [2 H, d, *J*(H3P) 21.5 Hz, P—$C\underline{H}_2$], 3.87 (4 H, m, $OC\underline{H}_2CH_3$). ^{13}C{^{1}H}-NMR (DMSO-d$_6$) δ_C: 16.19 [2 C,

J(C1P) 6.0 Hz, $\underline{C}H_3CH_2O$], 32.52 [1 C, J(C3P) 131.48 Hz, P—$\underline{C}H_2$], 35.10 (1 C, N—$\underline{C}H_3$), 37.88 (1 C, N—$\underline{C}H_3$), 61.63 [2 C, J(C2P) 6.0 Hz, $CH_3\underline{C}H_2O$], 164.45 [1 C, J(C4P) 5.2 Hz, $\underline{C}$=O]. $^{13}P\{^1H\}$-NMR (DMSO-d_6) δ_P: 23.18 ppm.

^1H-NMR (CH_3COCH_3-d_6) δ_H: 1.33 (6 H, t, $C\underline{H}_3CH_2O$), 3.03 [3 H, d, J(H6P) 1.22 Hz, N—$C\underline{H}_3$), 3.24 (3 H, s, N—$C\underline{H}_3$), 3.40 [2 H, d, J(H3P) 21.73 Hz, P—$C\underline{H}_2$], 4.23 (4 H, m, $CH_3C\underline{H}_2O$]. $^{13}C\{^1H\}$-NMR (CH_3COCH_3-d_6) δ_C: 16.49 [2 C, J(C1P) 5.98 Hz, $\underline{C}H_3CH_2O$], 30.81 [1 C, J(C3P) 134.2 Hz, P—$\underline{C}H_2$], 36.42 (1 C, N—$\underline{C}H_3$), 38.67 (1 C, N—$\underline{C}H_3$), 64.66 [2 C, J(C2P) 5.98 Hz, $CH_3\underline{C}H_2O$], 168.28 (1C, $\underline{C}$O). $^{31}P\{^1H\}$-NMR (CH_3COCH_3-d_6) δ_P: 25.94 ppm.

Diethyl Ester of 2-Dimethylamino-2-oxoethylphosphonic Acid

*Samarium (III) nitrate $SmL_2(NO_3)_3$ (**3b**).* 0.446 g (2 mmol) **1** and 0.444 g (1 mmol) $Sm(NO_3)_3{\cdot}6H_2O$ **2b** were reacted to give 0.700 g (89%) product with m.p. 126–128°C. After recrystallization from i-PrOH the m.p. of **3b** was 127–128.5°C, yield 0.626 g (80%). Found: C, 24.87; H, 5.19; N, 8.70. $C_{16}H_{36}N_5O_{17}P_2Sm$ (782.79) requires C, 24.55; H, 4.64; N, 8.95%. IR: ν_{max}(nujol)/cm^{-1}: 1020 and 1060 (P—O—C), 1210 (P=O), 1620 (C=O). ^1H-NMR (DMSO-d_6) δ_H: 1.07 (6 H, t, $C\underline{H}_3CH_2O$), 2.67 (3 H, s, N—$C\underline{H}_3$), 2.87 (3 H, s, N—$C\underline{H}_3$), 2.96 [2 H, J(H3P) 21.50 Hz, P—$C\underline{H}_2$], 3.87 (4 H, m, $CH_3C\underline{H}_2O$). $^{13}C\{^1H\}$-NMR (DMSO-d_6) δ_C: 16.22 [2 C, J(C1P) 6.1 Hz, $\underline{C}H_3CH_2O$], 32.46 [1 C, J(C3P) 132.83 Hz, P—$\underline{C}H_2$], 35.13 (1 C, N—$\underline{C}H_3$), 37.91 (1 C, N—$\underline{C}H_3$), 61.67 [2 C, J(C2P) 6.0 Hz, $CH_3\underline{C}H_2O$], 164.45 [1 C, J(C4P) 5.2 Hz, $\underline{C}$=O]. $^{31}P\{^1H\}$-NMR (DMSO-d_6) δ_P: 23.20 ppm.

^1H-NMR (CH_3COCH_3-d_6) δ_H: 1.38 [6 H, t, J(HH) 7.02 Hz, $C\underline{H}_3CH_2$—O], 2.94 [3 H, d, J(H6P) 0.93 Hz, N—CH_3], 3.31 (3 H, N—$C\underline{H}_3$), 3.85 [2 H, J(H3P) 21.75 HZ, P—$C\underline{H}_2$], 4.39 (4 H, m, $CH_3C\underline{H}_2O$). δ_C: 17.18 [2 C, J(C1P) 6.07 Hz, $\underline{C}H_3CH_2O$], 32.19 [1 C, J(C3P) 140.03 Hz, P—$\underline{C}H_2$], 37.03 (1 C, N—$\underline{C}H_3$), 39.43 (1 C, N—$\underline{C}H_3$), 65.69 [2 C, J(H2P) 6.29 Hz, $CH_3\underline{C}H_2O$], 169.12 [1 C, J(C4P) 4.55 Hz, $\underline{C}$=O]. $^{31}P\{^1H\}$-NMR (CH_3COCH_3-d_6) δ_P: 25.90 ppm.

Diethyl Ester of 2-Dimethylamino-2-oxoethylphosphonic Acid

*Ytterbium nitrate. $YbL_2(NO_3)_3$ (**3c**).* From 0.446 g (2 mmol) **1** and 0.450 g (1 mmol) $Yb(NO_3)_3{\cdot}5H_2O$ **2c**, 0.800 g oily product was obtained. After washing with i-PrOH 0.630 g (78%) **3c** was isolated as colorless oil. Found: C, 24.43; H, 4.75; N, 8.50. $C_{16}H_{36}N_5O_{17}P_2Yb$ (805.47) requires C, 23.86; H, 4.50; N, 8.69%. IR: ν_{max}(film)/cm^{-1} 1030 and 1060 (P—O—C), 1210 (P=O), 1630 (C=O).

Diethyl Ester of 2-Dimethylamino-2-oxoethylphosphonic Acid

*Erbium (III) nitrate $ErL_2(NO_3)_3$ (**3d**).* 0.446 g (2 mmol) **1** and 0.443 g (1 mmol) $Er(NO_3)_3{\cdot}5H_2O$ **2b** were reacted to give 0.780 g oily product. After washing with i-PrOH 0.700 g (87.5%) **3d** was isolated as a rose-colored oil. This oil crystallized after long staying, m.p. 68–69°C. Found: C, 23.78; H, 4.46; N, 8.61. $C_{16}H_{36}N_5O_{17}P_2Er$ (799.61) requires C, 24.03; H, 4.54; N, 8.76. IR: ν_{max}(nujol)/cm^{-1} 1020 and 1060 (P—O—C), 1200 (P=O), 1630 (C=O).

Diethyl Ester of 2-Dimethylamino-2-oxoethylphosphonic Acid

*Cerium (III) nitrate $CeL_2(NO_3)_3$ (**3e**).* Using the general procedure from 0.670 g (3 mmol) **1** and 0.434 g (1 mmol) $Ce(NO_3)_3{\cdot}6H_2O$ **2e**, 0.700 g (91%) white crystalline product with m.p. 144–145°C was obtained. After washing with hexane the m.p. of **3e** was 144.5–145.5°C (yield 0.673 g, 87%). Found: C, 25.20; H, 5.01; N, 8.89. $C_{16}H_{36}N_5O_{17}P_2Ce$ (772.55) requires C, 24.88; H, 4.70; N, 9.07%. IR: ν_{max}(nujol)/cm^{-1} 1020 and 1060 (P—O—C), 1210 (P=O), 1620 (C=O).

Diethyl Ester of 2-Dimethylamino-2-oxoethylphosphonic Acid

*Europium (III) nitrate $EuL_2(NO_3)_3$ (**3f**).* From **1** (0.446 g, 2 mmol) and $Eu(NO_3)_3{\cdot}6H_2O$ **2f** (0.461 g, 1 mmol), a white crystalline product (0.600 g, 76.5%) was obtained with m.p. 118–119°C. After recrystallization from i-PrOH the m.p. of **3f** was 119–120°C (0.442 g, 56%). Found: C, 24.88; H, 4.91; N, 8.52. $C_{16}H_{36}N_5O_{17}P_2Eu$ (784.31) requires C, 24.50; H, 4.63; N, 8.93%. IR.: ν_{max} (nujol)/cm^{-1} 1020 and 1060 (P—O—C), 1220 (P=O), 1620 (C=O). ^{1}H-NMR (CH_3COCH_3-d_6) δ_H: 1.08 [6 H, t, *J*(HH) 6.94 Hz, $C\underline{H}_3CH_2O$], 1.97 [2 H, *J*(H3P) 21.87 Hz, P—$C\underline{H}_2$], 2.74 (3 H, N—$C\underline{H}_3$), 3.29 (3 H, N—$C\underline{H}_3$), 3.55 (4 H, m, $CH_3C\underline{H}_2O$). ^{13}C-NMR (CH_3COCH_3-d_6) δ_C: 16.81 [2 C, *J*(C1P) 6.06 Hz, $\underline{C}H_3CH_2O$], 35.23 [1 C, *J*(C3P) 140.25 Hz, P—$\underline{C}H_2$], 36.96 (1 C, N—$\underline{C}H_3$), 37.06 (1 C, N—$\underline{C}H_3$), 65.04 [2 C, *J*(C2P) 6.29 Hz, $CH_3\underline{C}H_2O$], 142.54 (1 C, $\underline{C}$=O). ^{31}P{^{1}H}-NMR (CH_3COCH_3-d_6) δ_P: −47.50 ppm.

Diethyl Ester of 2-Dimethylamino-2-oxoethylphosphonic Acid

*Gadolinium (III) nitrate $GdL_2(NO_3)_3$ (**3g**).* From 0.464 g (2.08 mmol) **1** and 0.316 g (0.7 mmol) $Gd(NO_3)_3{\cdot}6H_2O$ **2g**, 0.400 g product with m.p. 98–103°C was isolated. After recrystallization from i-PrOH the m.p. of **3g** (white crystals) was 112.5–114°C (0.296 g, 53.5%). Found: C, 24.30; H, 4.47; N, 9.05. $C_{16}H_{36}N_5O_{17}P_2Gd$ (789.68) requires C, 24.34; H, 4.59;

N, 8.87%. IR: ν_{max}(nujol)/cm^{-1} 1020 and 1060 (P—O—C), 1220 (P=O), 1620 (C=O).

Diethyl Ester of 2-Dimethylamino-2-oxoethylphosphonic Acid 1 (L)

IR: ν_{max}(film)/cm^{-1} 1020 and 1060 (P—O—C), 1280 (P=O), 1670 (C=O). ^{1}H-NMR (DMSO-d$_6$) δ_H: 1.20 (6 H, t, $C\underline{H}_3CH_2O$), 2.78 [3 H, d, *J*(H6P) 1.3 Hz, N—$C\underline{H}_3$], 3.00 (3 H, s, N—$C\underline{H}_3$), 3.09 [2 H, d, *J*(H3P) 21.6 Hz, P—$C\underline{H}_2$], 4.00 (4 H, m, $CH_3C\underline{H}_2O$). ^{13}C{^{1}H}-NMR (DMSO-d$_6$) δ_C: 16.17 [2 C, *J*(C1P) 6.0 Hz, $\underline{C}H_3CH_2O$], 32.45 [1 C, *J*(C3P) 132.50 Hz, P—$\underline{C}H_2$], 35.12 (1 C, N—$\underline{C}H_3$), 37.90 (1 C, N—$\underline{C}H_3$), 61.65 [2 C, *J*(C2P) 6.0 Hz, $CH_3\underline{C}H_2$—O], 164.49 [1 C, *J*(C4P) 5.0 Hz, $\underline{C}$=O]. ^{31}P{^{1}H}-NMR (DMSO-d$_6$) δ_P: 23.19 ppm.

^{1}H-NMR (CH$_3$COCH$_3$-d$_6$) δ_H: 1.28 (6 H, t, $C\underline{H}_3CH_2O$), 2.89 [3 H, d, *J*(H6P) 1.46, N—$C\underline{H}_3$], 3.05 [2 H, d, *J*(H3P) 21.71 Hz, P—$C\underline{H}_2$], 3.13 (3 H s, N—$C\underline{H}_3$), 4.09 (4 H, m, $CH_3C\underline{H}_2O$). ^{13}C{^{1}H}-NMR (CH$_3$COCH$_3$-d$_6$) δ_C: 16.63 [2 C, *J*(C1P) 5.98 Hz, $\underline{C}H_3CH_2O$], 33.74 [1 C, *J*(C3P) 131.6 Hz, P—$\underline{C}H_2$], 35.49 (1 C, N—$\underline{C}H_3$), 38.46 (1 C, N—$\underline{C}H_3$), 62.60 [2 C, *J*(C2P) 5.98 Hz, $CH_3\underline{C}H_2O$], 165.10 (1 C, $\underline{C}$O). ^{31}P{^{1}H}-NMR (CH$_3$COCH$_3$-d$_6$) δ_P: 22.38 ppm.

X-RAY EXPERIMENTAL

Suitable crystals were obtained by recrystallization from i-PrOH. The data were collected on a Hilger & Watts (Y290) diffractometer using Mo-Kα radiation from prismatic crystal with size $0.60 \times 0.60 \times 0.30$ mm at 153 K. The cell parameters were obtained from the positions of 25 reflections with $20^\circ \leq 2\theta \leq 22^\circ$. 10099 reflections were measured. After averaging of the symmetrically equivalent reflections 7323 unique reflections were obtained; 5762 with $I > 2\sigma(I)$. Direct methods SHELXS-97[16] and successive interpretation of difference Fourier maps, followed by least-squares refinement SHELXL-97[17] solved the structure. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions using isotropic parameters. The details of the data collection and refinement are summarized in Table I.*

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*Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 151197. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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