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Complexes of Diethyl-2-amino-2-oxoethylphosphonate with Lanthanide Nitrates

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ABSTRACT: *Lanthanide complexes $LnL_2(NO_3)_3$* **3a–f** *are obtained where Ln is La, Ce, Sm, Eu, Er, and Yb and L is the diethyl 2-amino-2-oxoethylphosphonate. They were characterized by elemental analysis, IR, and NMR spectroscopy. Monodentate coordination by the phosphoryl group is suggested for the ligand on the basis of the spectral data. The stabilization is achieved by including a molecule of the solvent in the complexes* **3a–d**. © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:128–131, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10112

INTRODUCTION

In the recent years there has been a considerable interest in the use of ligands containing different donor atoms for coordination of lanthanide metal ions. The group of carbamoylmethylphosphonates (2-amino-2-oxoethylphosphonates and derivatives) appears to be closely related to β-diketones. They provide a system in which a variety of metal–ligand bonding may be studied [1–5]. These mixed ligands containing P=O, and N—C=O donor groups are widely used for extraction and separation of ions [6–8] related to nuclear fuels processing. The type of coordination and the coordination numbers depend strongly on the metal salts, as well as on the substituents of the phosphorus and amide nitrogen atoms [1–5]. In our previous work we described the synthesis and structures of complexes of lanthanide elements with 2-oxo-phosphonates and phosphine oxides [9] as well as of 2-dimethylamino-2-oxoethylphosphonates [10]. Herein we report the preparation and characterization of the complexes of diethyl 2-amino-2-oxoethylphosphonate (**1**) with lanthanide nitrates **2**. The coordination properties of this unsubstituted carbamoylmethyl-phosphonate are less studied and are interesting because of the weak affinity of one of its donor sites towards the acceptor. The complexes obtained from such ligands (so called hemilabile ligands) should be potential catalytic precursors in synthetic processes [11].

RESULTS AND DISCUSSION

The lanthanide complexes **3a–f** were obtained from the diethyl 2-amino-2-oxoethylphosphonate **1** (L) and the lanthanide nitrates **2a–f** in a ratio L/**2** 2:1 at room temperature in ethanol. The crude products

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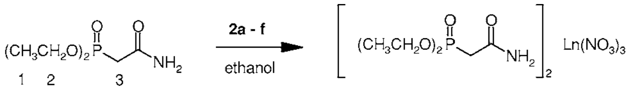
are colorless oils; only **3e** is rose colored. After treating with isopropanol (see Experimental section), complexes with the lighter lanthanides (**3a–c**) crystallize. Complexes **3a–f** are well soluble in water, methanol, DMSO, and acetone and less soluble in alcohol, chloroform, diethyl ether, and hexane. The elemental analysis confirmed a molecular formula $LnL_2(NO_3)_3$ where L is $(C_2H_5O)_2P(O)CH_2CONH_2$ and Ln is La, Sm, Yb, Er, Ce, and Eu (Scheme 1). In complexes **3a–d** one molecule of isopropanol is obviously included during the purification of the crude product.

IR spectra of complexes **3a–f**, measured in KBr (tablet), showed an absorption at 1193–1200 cm^{-1} for the PO vibrations; thus the complexation with the P=O group produced a low-frequency shift of 42–49 cm^{-1} in respect to **1** (ν_{PO} 1242 cm^{-1}) (see Table 1). This is in agreement with the data for lanthanide complexes with other carbamoyl phosphonate ligands [3,4,10]. The assignment of the amide $CONH_2$ frequency is complicated. The starting ligand **1** contains only one strong broad band at 1666 cm^{-1} corresponding to the C=O vibrations (ν_{CO}, "first amide band") and N—H deformation vibrations (δ_{NH}, "second amide band") for an associated NH_2 group. In complexes **3a–f** two bands are present in this region: 1598–1605 (m) and 1660–1669 cm^{-1} (s). We assign the band at 1660–1669 cm^{-1} to ν_{CO} and the band 1598–1605 cm^{-1} to the δ_{NH} (not associated). The absence of a low-frequency shift of the band for C=O vibration in **3a–f** suggests monodentate coordination of the ligand **1** only by the P=O group. The characterization of the nitrate groups in KBr is made on the presence of bands for $\nu_{N=O}$ at about 1450, 1300, and 820 cm^{-1} (see Table 1), which is in accordance with the data for analogous complexes, containing bidentate nitrogroups [10,12,13]. An absence of the peak at around 1290 cm^{-1} is considered as an indication of monodentate nature of the nitrate ion [12]. The NMR spectra were recorded in methanol and acetone, where the complexes **3** seem to be stable. In DMSO the equilibrium is shifted in direction to the free ligand **1**, which was proved by the identity of the ^1H NMR spectra of the ligand **1** and the lanthanide complex **3a**. Complexes **3d, 3e**, and **3f** are paramagnetic. The spectra of **3a–d** contain signals of included isopropanol at $\delta = 1.15$ and 3.93 ppm (in methanol). The signals for H3 and C3 (P—$\underline{CH_2}$) in methanol are not well resolved because of a slow exchange of the two protons, which is due to some flexibility around the central unit. The signal of C3 is not observed in some other carbamoylmethylphosphonate complexes as well [3]. ^{31}P, ^{13}C and ^1H NMR spectra of **3a, 3b**, and **3c** showed shifts downfield from the free ligand (see Table 2 for ^{13}C and Experimental section for ^1H), most significant by **3b** in methanol ($\Delta\delta$ C2 = 3.27 ppm, $\Delta\delta$ C=O = 6.35 ppm, and $\Delta\delta$ ^{31}P = 6.03 ppm).



1

3a - f

2a: $La(NO_3)_3.6H_2O$
2b: $Ce(NO_3)_3.6H_2O$
2c: $Sm(NO_3)_3.6H_2O$
2d: $Eu(NO_3)_3.6H_2O$
2e: $Er(NO_3)_3.5H_2O$
2f: $Yb(NO_3)_3.5H_2O$

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

Comparison with the shifts of the corresponding diethyl-2-dimethylamino-2-oxoethylphosphonate lanthanide nitrates (**4**) [10] indicates weaker coordination of the ligand in **3**. On the basis of these data, combined with the IR spectra we suggest monodentate coordination of ligand **1** with lanthanide ions by the phosphonate oxygen. This rare kind of binding could be explained with the lower electron density on the amide oxygen in respect to the *N*-dimethylamidophosphonate complexes. The stabilization arises probably from the coordination of the metal with the oxygen of the solvent, thus decreasing the coordination number by 1 (9 in complexes of **3** and by 10 in **4** [10]). Horwitz and co-workers [14] have suggested that monodentate coordination through metal-phosphoryl oxygen occurs in solution of the complexes of dihexyl *N,N*-diethyl-carbamoylmethylenephosphonate (DHDECMP) with lanthanide and actinide ions. Similar monodentate coordination of the ligand and stabilization by a molecule of water is described for the complex of $Er(NO_3)_3$ and diisopropyl *N*-diethyl-carbamoylmethylphosphonate (DiDECMP) [3]. Unfortunately, till now we could not confirm the structure of the complexes **3** by X-ray diffraction analysis.

EXPERIMENTAL

Ligand **1** was prepared and purified according to the literature [15]. Commercial lanthanide nitrates and anhydrous ethanol were used. Analytical data were obtained from the Microanalytical Laboratory of the Department of Chemistry, University of Sofia. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on a VARIAN Gemini 200 BB or a BRUKER DRX-250 in either 5- or 10-mm tubes at room temperature. ^1H 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 multiplicities were determined via APT or DEPT

TABLE 1 Selected IR Absorptions (cm^{-1}) for Complexes **3a–f** and Ligand **1** in Tablet KBr

Compound	$\nu_{P—O—C}$	$\nu_{P=O}$	$\nu_{C=O} + \delta_{NH}$	ν_{NO}
1	1028, 1049s	1242 s	1666 br	
3a	1020 br	1200 s	1598 m, 1660 s	815 m, 1300 s, 1430 s
3b	1026 br	1197 s	1602 m, 1666 s	819 m, 1293 s, 1449 s
3c	1026 br	1197 s	1605 m, 1664 s	819 m, 1299 s, 1443 m
3d	1025 br	1199 s	1605 m, 1667 s	817 m, 1301 s, 1444 s
3e	1026 br	1196 s	1603 m, 1667 s	816 m, 1298 s, 1443 m
3f	1024 br	1193 s	1603 m, 1669 s	815 m, 1293 s, 1445 s

spectra [16]. The integral values are given for one ligand of the molecule. The IR spectra were registered on Perkin-Elmer 983G equipment.

Synthesis of Complexes 3a–f

General Procedure. A solution of lanthanide nitrate **2** (1 mmol) in 4 ml of ethanol was added to diethyl-2-amino-2-oxoethylphosphonate **1** (0.390 g, 2 mmol) in 2 ml of the same solvent. The reaction mixture was stirred for 1 h at room temperature, the solvent was evaporated in vacuum, and the obtained oily product was washed with ethyl acetate and dissolved in isopropanol. After cooling, the crystalline products were filtered off (the oily products were purified by decantation) and dried in vacuum.

*Diethyl-2-amino-2-oxoethylphosphonate Lanthanum(III) Nitrate $LaL_2(NO_3)_3\cdot(CH_3)_2CHOH$ (***3a***).* Using the general procedure, from **1** and **2a** (0.433 g), after treatment with *i*-PrOH, 0.433 g (56%) white crystalline **3a** with mp 101–105°C was obtained. Found: C, 23.40; H, 4.91; N, 9.13. $C_{12}H_{28}N_5O_{17}P_2La\cdot(CH_3)_2CHOH$ (775.33) requires C, 23.24; H, 4.68; N, 9.03%. ^{1}H NMR (CD_3OD) δ: 1.15 [6 H, d, J(HH) 6.0 Hz, $(C\underline{H}_3)_2CHOH$)], 1.36 (6 H, t, J(HH) 7 Hz, $C\underline{H}_3CH_2O$), 3.08 [2 H, d, J(HP) 21.7 Hz, $P—C\underline{H}_2$], 3.93 [1 H, m, $(CH_3)_2C\underline{H}$]. 4.21 (4 H, m, J(HH) 7.0 Hz, J(HP) 0.9 Hz, $OC\underline{H}_2CH_3$). $^{13}C\{^1H\}$ NMR (CD_3OD) δ: 16.51 [d, J(CP) 5.9 Hz, $\underline{C}H_3CH_2O$], 25.23[s, $(\underline{C}H_3)_2CHOH$], 65.05 [J(CP) 6.1 Hz, $CH_3\underline{C}H_2O$], 171.07 [s, $\underline{C}{=}O$].

^{1}H NMR (acetone-d_6) δ: 1.10 [6 H, d, J(HH) 6.10 Hz, $(C\underline{H}_3)_2CH$], 1.33 (6 H, t, J(HH) 7.1 Hz, $C\underline{H}_3CH_2O$), 3.18 [2 H, d, J(HP) 21.49 Hz, $P—C\underline{H}_2$], 4.22 (4 H, m, $CH_3C\underline{H}_2O$].

*Diethyl-2-amino-2-oxoethylphosphonate Cerium-(III) Nitrate $CeL_2(NO_3)_3\cdot(CH_3)_2CHOH$ (***3b***).* Using the general procedure from **1** and **2b** (0.430 g) 0.660 g (85%) white crystalline **3b** with mp 45–53°C was obtained. After recrystallization from *i*-PrOH, the mp was 98–99°C (yield 0.528 g, 68%). Found: C, 23.55; H, 5.41; N, 9.50. $C_{12}H_{28}N_5O_{17}P_2Ce\cdot(CH_3)_2CHOH$(776.54) requires C, 23.20; H, 4.67; N, 9.02%. ^{1}HNMR (CD_3OD) δ: 1.16 [6 H, d, J(HH) 6.20 Hz, $(C\underline{H}_3)_2CHOH$)], 1.71 [6 H, t, J (HH) 7.0 Hz, $C\underline{H}_3CH_2O$], 3.93[1 H, m, J (HH) 6.2 Hz, $(CH_3)_2C\underline{H}$], 5.05 (4 H, m, $CH_3C\underline{H}_2O$). $^{13}C\{^1H\}$ NMR (CD_3OD) δ: 17.01 [J(CP) 6.0 Hz, $\underline{C}H_3CH_2O$], 25.26 [s, $(\underline{C}H_3)_2CHOH$], 66.09 [J(CP) 6.3 Hz, $CH_3\underline{C}H_2O$], 175.72 (s, $\underline{C}{=}O$).

TABLE 2 Selected NMR Data for Complexes **3a–f** and Ligand **1**

Compound	$\delta(^{31}P)$	$W_{1/2}$(Hz)	$\delta(^{13}CH_3)$	$\delta(^{13}CH_2O)$	$\delta(P^{13}CH_2)$	$\delta(^{13}C{=}O)$
1 (CD_3OD)	23.94		16.60	64.08	35.35	169.37
1 (acetone-d_6)	23.47		15.85	61.94	34.74	165.87
3a (CD_3OD)	24.19	7.4	16.51	65.05	25.23	171.07
3a (acetone-d_6)	24.84	8.5				
3b (CD_3OD)	29.97	12.8	17.01	66.09	25.26	175.72
3b (acetone-d_6)	39.37	16.0				
3c (CD_3OD)	25.28	8.6	15.30	63.88	23.94	
3c (acetone-d_6)	25.07	8.0				
3d (CD_3OD)	−7.94	180				
3d (acetone-d_6)	−47.5	212				
3e (CD_3OD)	−26	1980				
3f (CD_3OD)	5.13	85				
3f (acetone-d_6)	−9.25	260				

*Diethyl-2-amino-2-oxoethylphosphonate Samarium(III) Nitrate $SmL_2(NO_3)_3\cdot(CH_3)_2CHOH$ (**3c**).* Using the general procedure, 0.585 g (3 mmol) **1** and 0.666 g (1.5 mmol) **2c** were reacted to give 0.870 g (74%) **3c** with mp 40–45°C. After recrystallization from *i*-PrOH, the mp was 66–67°C, yield 0.370 g (31%). Found: C, 20.99; H, 5.13; N, 8.66. $C_{12}H_{28}N_5O_{17}P_2Sm\cdot 2H_2O \cdot (CH_3)_2CHOH$ (822.81) requires C, 21.90; H, 4.90; N, 8.51%. ^{1}H NMR (CD_3OD) δ: 1.14 [6 H, d, J(HH) 6.10 Hz, $(C\underline{H}_3)_2CHOH)$], 1.38 (6 H, t, J(HH) 6.9 Hz, $C\underline{H}_3CH_2O$), 3.92[1 H, m, $(CH_3)_2C\underline{H}$], 4.29 (4 H, m, $CH3C\underline{H}_2O$). $^{13}C\{^1H\}$ NMR (CD_3OD) δ: 15.30 [J(CP) 5.98 Hz, $\underline{C}H_3CH_2O$], 23.94 [s, $(\underline{C}H_3)_2CHOH$], 63.88 [$CH_3\underline{C}H_2O$]. ^{1}H NMR (CH_3COCH_3-d_6) δ: 1.10 [6 H, d, J(HH) 6.35 Hz, $(C\underline{H}_3)_2CH$],1.38 [6 H, t, J(HH) 7.08 Hz, $C\underline{H}_3CH_2$—O], 3.51 [2 H, J(HP) 21.49 Hz, P—$C\underline{H}_2$], 3.89 [1 H, m, $(CH_3)_2C\underline{H}$], 4.37 (4 H, m, $CH_3C\underline{H}_2O$).

*Diethyl-2-amino-2-oxoethylphosphonate Europium(III) Nitrate $EuL_2(NO_3)_3\cdot(CH_3)_2CHOH$ (**3d**).* Using the general procedure, from **1** and **2d** (0.430 g), a colorless oily product (0.700 g, 89%) was obtained. After washing with *i*-PrOH the yield of **3d** (oil) was 0.370 g (47%). Found: C, 23.52; H, 5.19; N, 8.91. $C_{12}H_{28}N_5O_{17}P_2Eu\cdot(CH_3)_2CHOH$ (788.385) requires C, 22.85; H, 4.60; N, 8.88%.), ^{1}H NMR (acetone-d_6) δ: 1.09 (6 H, t, J(HH) 6.84, $C\underline{H}_3CH_2O$), 2.33 [2 H, d, J(HP) 21.73 Hz, P—$C\underline{H}_2$], 3.53 (4 H, m, $CH_3C\underline{H}_2O$).

*Diethyl-2-amino-2-oxoethylphosphonate Erbium-(III) Nitrate $ErL_2(NO_3)_3$ (**3e**).* Using the general procedure, 0.585 g (3 mmol) **1** and 0.660 g (1 mmol) **2e** were reacted to give 1.160 g (96%) oily product. After washing with CH_2Cl_2 and then with *i*-PrOH, 0.350 g (29%) **3e** was isolated as a rose-colored oil. Found: C, 19.54; H, 4.03; N, 8.71. $C_{12}H_{28}N_5O_{17}P_2Er$ (743.59) requires C, 19.38; H, 3.80; N, 9.42.

*Diethyl-2-amino-2-oxoethylphosphonate Ytterbium Nitrate $YbL_2(NO_3)_3$ (**3f**).* Using the general procedure, from 0.585 g (3 mmol) **1** and 0.675 g (1.5 mmol) **2f**, 1.220 g oily product was obtained. After washing with CH_2Cl_2 and then with *i*-PrOH, 0.965 g (80%) **3f** was isolated as colorless oil. Found: C, 18.97; H, 4.10; N, 9.32. $C_{12}H_{28}N_5O_{17}P_2Yb$ (749.37) requires C, 19.23; H, 3.77; N, 9.35%.

*Diethyl-2-amino-2-oxoethylphosphonate (**1**).* ^{1}H NMR (CD_3OD) δ: 1.34 [6 H, dt, J(HH) 7.1 Hz, J(HP) 0.5 Hz, $C\underline{H}_3CH_2O$), 2.95 [2 H, d, J(HP) 21.9 Hz, P—$C\underline{H}_2$], 4.16 [4 H, m, J(HH) 7.1 Hz, J(HP) 0.6 Hz, $CH_3C\underline{H}_2O$). $^{13}C\{^1H\}$ NMR (CD_3OD) δ: 16.60 [J(CP) 6.1 Hz, $\underline{C}H_3CH_2O$], 35.35 [J(CP) 134.50 Hz, P—$\underline{C}H_2$], 64.08 [J(CP) 6.4 Hz, $CH_3\underline{C}H_2$—O], 169.37 [$\underline{C}$=O]. ^{1}H NMR (acetone-d_6) δ: 1.28 (6 H, t, J(HH)7.08, $C\underline{H}_3CH_2O$), 2.89 [2 H, d, J(HP) 21.24 Hz, P—$C\underline{H}_2$], 4.11 (4 H, m, J(HH) 7.08 Hz, J(HP) 8.12 Hz, $CH_3C\underline{H}_2O$), 6.49 (1 H, s, N—$\underline{H}$), 6.97 (1 H, s, N—$\underline{H}$). $^{13}C\{^1H\}$ NMR (acetone-d_6) δ: 15.85 [2 C, J(C1P) 6.19 Hz, $\underline{C}H_3CH_2O$], 34.74 [1 C, J(CP) 130.03 Hz, P—$\underline{C}H_2$], 61.94 [2 C, J(CP) 6.13 Hz, $CH_3\underline{C}H_2O$], 165.87 (1 C, $\underline{C}$=O).

REFERENCES

[1] Siddall, T. H., III. J Inorg Nucl Chem 1963, 25, 883–892.
[2] Stewart, W. E.; Siddall, T. H. J Inorg Nucl Chem 1970, 32, 3599–3604.
[3] Bowen, S. M.; Duesler, E. N.; Paine, R. T. Inorg Chim Acta 1982, 61, 155–166.
[4] Bowen, S. M.; Duesler, E. N.; Paine, R. T. Inorg Chem 1982, 21, 261–265.
[5] Bowen, S. M.; Duesler, E. N.; Paine, R. T. Inorg Chem 1983, 22, 286–90.
[6] (a) Hagan, P. G.; Navratil, J. D. Energy Res Abstr 1978, 3, Abstr. No. 32826; (b) Hagan, P. G.; Navratil, J. D. Report REP-2708, 1978; CA 90: 11765u.
[7] (a) Horwitz, E. P.; Kalina, D. G.; Muscatello, A. C. Sep Sci Technol 1981, 16, 403–416; CA 94: 215306f; (b) Horwitz, E. P.; Mason, G. W. US Patent Application 928,026, 29 Feb. 1980; CA 92: 205791e.
[8] (a) Endo, Y. Jpn Kokai Tokkio Koho JP 63,208,799, 30 Aug. 1988; CA 110: 103728n; (b) Endo, Y. Jpn Kokai Tokkio Koho JP 63,208,800, 30 Aug. 1988; CA 110: 123537c; (c) Endo, Y. Jpn Kokai Tokkio Koho JP 63,208,798, 30 Aug. 1988; CA 111: 30104q.
[9] Petrova, J.; Haupt, E. T. K.; Momchilova, S.; Zdravkova, Z. Synth React Inorg Met -Org Chem 1999, 29, 1641–1654.
[10] Petrova, J.; Momchilova, S.; Haupt, E. T. K.; Kopf, J.; Eggers, G. Phosphorus Sulfur Silicon 2002, 177, 1337–1347.
[11] Minghetti, G.; Stoccoro, S.; Cinellu, M. A.; Zucca, A.; Manassero, M.; Sansoni, M. J Chem Soc, Dalton Trans 1998, 4119–4126.
[12] Nagar, M. S.; Ruikar, P. B.; Mathur, J. N.; Iyer, R. H. Synth React Inorg Met -Org Chem 1998, 28, 621–636.
[13] Siddall, T. H., III; Mc Donald, R. L.; Stewart, W. E. J. Mol Spectroscopy 1968, 28, 243–264.
[14] Horwitz, E. P.; Muscatello, A. C.; Kalina, D. G.; Kaplan, L. Sep Sci Tech 1981, 16, 417.
[15] Nylen, P. Berichte der Deutschen Chemischen Gesellschaft 1926, 59, 1119–1128.
[16] Patt, S. L.; Shoolery, J. N. J Magn Res 1982, 46, 535.