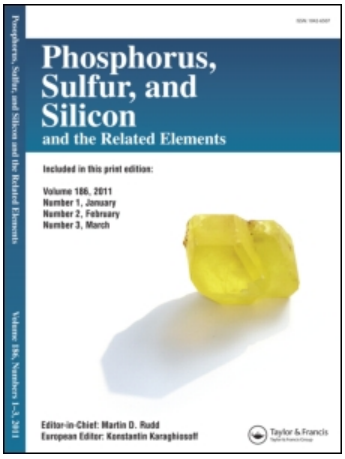

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Complexes of Lanthanide Nitrates with Alkyl Esters of Bromomethylenediphosphonic Acid

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Complexes of lanthanide nitrates (La, Ce, Sm, Gd, Er, and Yb) with tetraethyl and tetraisopropyl esters of bromomethylenediphosphonic acid were prepared. The complexes were characterized by elemental analysis, IR spectroscopy, and, in some cases, NMR. The data confirm that diphosphonates coordinate with two P=O groups, and there are no indications for the existence of noncoordinated P=O groups. The structure of the complexes depends only on the ionic radius of the central metal atom and not on changes in the electronic or steric behavior of the ester groups. For the complexes of La, Ce, Sm, and Gd nitrates, the formula is $LnL_2(NO_3)_3$, and for Er and Yb nitrates it is $Ln_2L_3(NO_3)_6$ (Ln=La, Ce, Sm, Gd, Er, Yb; L = diphosphonate).

Keywords Complexes; esters of bromomethylenediphosphonic acid; lanthanide nitrates

INTRODUCTION

Complexes of lanthanides and P=O groups containing chelating ligands such as $Ph_2P(O)CH_2P(O)Ph_2$ [1–3] and $(RO)_2P(O)CH_2P(O)(OR)_2$ are attracting interest in the field of catalysis,[4] in mimics for less accessible actinide complexes of potential interest in nuclear waste treatment,[5–9] and for basic structural investigations.

Complexes of tetraisopropyl methylenediphosphonate and lanthanide nitrates have been described by Stewart and Siddall.[10] The structures of the complexes change from monomeric to dimeric due to the decrease of metal ion size. Complexes of the same ligand with lanthanum and praseodymium nitrates[11] were obtained with ligand:nitrate ratios of 2:1 and 1:1. On the other hand, the complexes

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with Ce, Pr, Nd, Dy, and Y have been determined with the formula $LnL_2(NO_3)_3$ (Ln = lanthanide and L = $(i\text{-}PrO)_2P(O)CH_2P(O)(Oi\text{-}Pr)_2$).[10,12] A study of complexes of $(EtO)_2P(O)CH_2P(O)(OEt)_2$ has also been reported.[13] X-ray diffraction analysis verifies that the nitrate groups in some of the obtained complexes are coordinated in a bidentate manner. Complexes of 2,4-bis(diphenylphosphorylmethyl)mesitylene with Ce, Nd, and Er nitrate were studied, and, again, two structures were obtained with 1:1 or 2:1 ratios (ligand:lanthanide nitrate).[14] Lanthanide nitrate complexes with $Ph_2P(O)CH_2CH_2P(O)Ph_2$ have been studied, and their polymeric structures have been confirmed by X-ray spectroscopy.[15] A similar structure was obtained by us in the complexes of lanthanide nitrates and ethylene diphosphonate esters.[16]

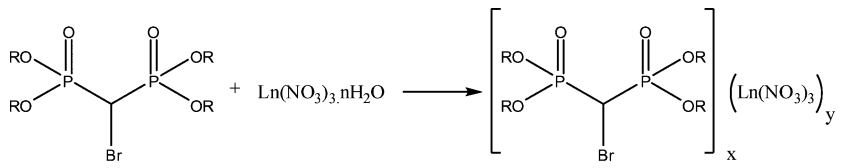
To investigate the possible influence of the variation of substituents in the methylene group of diphosphonates in more detail, we prepared complexes of alkyl esters of ethylidenediphosphonic acids with lanthanide nitrates.[17] We obtained a single crystal of the complex of $Dy(NO_3)_3$ with $CH_2[P(O)(Oi\text{-}Pr)_2]_2$, and the X-ray analysis confirmed a structure with a 2:1 ratio.[13] It was proven that one of the nitrate groups is monodentate coordinated. In continuation of these studies, we present the results obtained for complexes of lanthanide nitrates with an electron-withdrawing bromo substituent in the methylene group of the diphosphonates.

RESULTS AND DISCUSSION

Synthesis

All complexes were synthesized by adding an ethanol solution of the corresponding lanthanide nitrate to the liquid diphosphonate (Scheme 1). After stirring the solution for 1 h, the ethanol was evaporated, and the resulting oil or the mixture of oil and crystals was treated with diethyl ether or a mixture of diethyl ether and hexane and cooled to 0°C. The resulting precipitate was filtered.

In some cases, the crystals were recrystallized (see the Experimental section). Elemental analysis proved the molecular formula of the complexes to be $LnL_2(NO_3)_3$ for the complexes of La, Ce, Sm, and Gd (**3a–d**, **5a–d**), and for the complexes of Er and Yb (**3e**,**f** and **5e**,**f**), the structure is $Ln_2L_3(NO_3)_6$, where L is one of the two ligands $BrCH[P(O)(OC_2H_5)_2]_2$ or $BrCH[P(O)(Oi\text{-}C_3H_7)_2]_2$. The complexes are white crystals (except for the complex with $Er(NO_3)_3$, which is pale pink); very soluble in ethanol, methanol, and chloroform; and less soluble in diethyl ether, petroleum ether, and hexane.



1: R = Et
4: R = i-Pr

2a: Ln = La; n = 6
2b: Ln = Ce; n = 6
2c: Ln = Sm; n = 6
2d: Ln = Gd; n = 6
2e: Ln = Er; n = 5
2f: Ln = Yb; n = 5

R = Et
3a: Ln = La; x = 2; y = 1
3b: Ln = Ce; x = 2; y = 1
3c: Ln = Sm; x = 2; y = 1
3d: Ln = Gd; x = 2; y = 1
3e: Ln = Er; x = 3; y = 2
3f: Ln = Yb; x = 3; y= 2

R = i-Pr
5a: Ln = La; x = 2; y = 1
5b: Ln = Ce; x = 2; y = 1
5c: Ln = Sm; x = 2; y = 1
5d: Ln = Gd; x = 2; y = 1
5e: Ln = Er; x = 3; y = 2
5f: Ln = Yb; x = 3; y= 2

SCHEME 1 Synthesis of the complexes **3a–f** and **5a–f**.

Infrared Spectra Analysis

The IR spectra of the complexes **3a–f** were recorded in nujol, $CHCl_3$, and as KBr pellets. The band for the ν(P=O) vibration is shifted to lower frequencies by 30–45 cm^{-1} compared to the free ligand **1** (ν(P=O) = 1255 cm^{-1}) in all recorded spectra. The broadened band for ν(P-O-C) is not shifted in the spectra of the complexes and remains at about 1020–1040 cm^{-1}. Thus, the coordination of the ligand **1** is accomplished through the two P=O groups. It is known that in metal complexes with nitrate groups, the nitrate has three observable bands ν(N=O) 1300–1600 cm^{-1}, ν(N-O) 1200–1400 cm^{-1}, and $\delta(NO_3)$ 700–800 cm^{-1}.[18] As it can be seen from the spectral data (see the Experimental section), in $CHCl_3$ only one band for the ν(N-O) (1300–1315 cm^{-1}) and one for ν(N=O) vibrations (1455—1495 cm^{-1}) is observed. The band for the N-O stretching vibration is not remarkably changed from La to Yb, but the band for the ν(N=O) is shifted to higher frequencies from La to Yb. This points to a bidentate coordination of the nitrate groups in the complexes **3a–f**.[19–21] In nujol only a band at 1310–1330 cm^{-1} is observed; the second band, which is expected to be at 1450–1500 cm^{-1}, is covered by a band from nujol. According to a study by Fawcett et al.,[21] if the nitrate groups are monodentate, there must be a band at 1370–1380 cm^{-1}; such a band is not observed in the spectra of the complexes. If there is mixed coordination of the nitrate groups, the IR spectra is not reliable to confirm the structure.[19] When the spectra of **3a–f** were recorded in KBr pellets, a new band appeared at 1385 cm^{-1}, which demonstrates that there are free NO_3^- groups. This observation confirms that the nitrate groups are displaced under high pressure, and it is not possible to obtain information for their coordination to the metal ion.

The IR spectra for the complexes **5a–f** were recorded in nujol and in KBr pellets. Again the band with the most remarkable variation is ν(P=O), which is shifted to lower frequencies by 40–50 cm^{-1}(see the Experimental section). The band for ν(P-O-C) is not influenced. There is a band for coordinated NO_3^- groups at about 1300 cm^{-1}(nujol). According to these data, the ligand **4** is coordinated by its two P=O groups to the metal in the complexes **5a–f**. The absence of a band for the monodentate nitrate group and the presence of the band at about 1300 cm^{-1} points to bidentate coordination of the nitrate groups in **5a–f**. Again there is a band at 1385 cm^{-1} in the spectra in KBr pellets, which is assigned to non-coordinated nitrate groups.

NMR Spectra Analysis

The NMR spectra (Table I) were recorded only for the complexes **3a–c** and **5a–c** because of the strong paramagnetism of the remaining lanthanides. In the ^{1}H NMR spectra, the most varied signal is due to the $P_2C\underline{H}Br$ proton ($\Delta = +0.60 \div +6.08$ ppm, for **3a–c** and **5a–c**), which confirms the coordination of the P=O group. Again, as it was previously observed,[17] the signal for ($P_2C\underline{H}Br$) in the complex of Ce is shifted more than in the spectra of La and Sm complexes ($\Delta = +4.43$ ppm for **3b** and +6.08 ppm for **5b**). There is some increase in the value of the ^2J(HP) coupling constant within 2 Hz for the same group. This indicates some steric changes of the ligands in the complexes compared to the non-coordinated molecules. The signal for the methyl groups (CH_3-C-O) is split in the spectra of the complexes into two (for **3a–c**) or into three or four resonances (for **5a–c**) compared to the free ligands **1** and **4**. There

TABLE I ^{1}H, ^{13}C, and ^{31}P Chemical Shifts and Coupling Constants of the P-CH-P Group in 1, 3a–c, 4, 5a–c

	P-C$\underline{H}$-P		P-$\underline{C}$H-P		^{31}P
	δ [ppm]	^2J(HP) [Hz]	δ [ppm]	^1J(CP) [Hz]	δ [ppm]
1[a]	3.81	17	29.6	142	14.0
3a	4.41	19.40	24.07	140.3	13.8
3b	8.24	16.28	26.36	140.3	34.2
3c	4.83	19.61	24.95	140.9	14.6
4[a]	3.72	17	31.5	144	12.3
5a	4.32	19.76	25.31	140.4	12.2
5b	9.80	19.57	29.86	140.7	35.6
5c	4.93	19.93	26.43	139.8	12.5

[a]Data is taken form lit. [22]

are also several signals for the C<u>H</u>-O groups ($CH_3C\underline{H}_2OP$ in **3a–c** and $(CH_3)_2C\underline{H}OP$ in **5a–c**) compared to the free ligands, where these protons are characterized by one group of signals. The analysis of the ^{13}C NMR spectra are in agreement with the conclusions from the ^{1}H NMR spectra. Again the most influenced signal is for the P-<u>C</u>-P group, confirming the participation of the P=O group in the coordination. The ^{31}P NMR spectrum only gave one signal, indicating that there are no alternate species of the diphosphonate complexes existing in solution.

The EPR analysis yields a signal only for the Gd complexes **3d** and **5d** in $CHCl_3$ solution. This signal disappears when the solution is frozen at liquid nitrogen temperature. No EPR signals are detected for complexes **3e**,**f** and **5e**,**f** because the f-electrons are shielded.

CONCLUSIONS

The structures of the complexes are not influenced by varying the bulkiness of the ester groups in the diphosphonates, which means that these groups are not sterically in close contact to the coordination center. The spectroscopic data clearly confirm that the decreasing ion radius of the lanthanide atom is the dominating factor for structural variations. The ligands compete for the available space and finally direct the structure to preferred lower coordination number. It was proven that the diphosphonate molecules in both cases (2:1 and 3:2) are coordinated by their two P=O groups in the solid state as well as in solution. According to the available IR data, the nitrate groups are bidentate-coordinated in all cases. That means that the coordination number is 10 for the complexes with La, Ce, Sm, and Gd nitrates and 9 for complexes with Er and Yb nitrates.

EXPERIMENTAL

Phosphonate ligands **1** and **4** were prepared according to a method in the literature.[22] Commercial lanthanide nitrates and anhydrous ethanol were used. Analytical data were obtained from the microanalytical laboratory of the Department of Chemistry, Sofia University "Sv. Kl. Ohridski." ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded at room temperature on a Bruker DRX-250 and a Bruker Avance 400. ^{1}H NMR spectra were referenced relative to internal TMS, ^{13}C NMR spectra to the corresponding solvent signal, and ^{31}P-NMR to external 85% aq. H_3PO_4. The IR spectra in nujol and CH_3Cl were recorded on SPECORD-71R spectrophotometer and the spectra in KBr discs Bruker Tensor-27. EPR spectra were recorded on a Bruker-B ER420 X-band EPR spectrometer.

General Procedure

A solution of lanthanide nitrate (0.5 mmol) in 0.5 mL ethanol was added to 2–2.5 mmol of liquid diphosphonate and an additional 0.5 mL ethanol was added. The reaction mixture was stirred for 60 min at room temperature. If the product did not crystallize, the ethanol was evaporated in vacuum, and the resulting oil was then treated with diethyl ether or mixture of diethyl ether with hexane and cooled (in most of the cases) to form a precipitate. The ^{31}P NMR data in $CDCl_3$ are collected in Table I.

Tetraethyl Ester of Bromomethylenediphosphonic Acid Lanthanum(III) Nitrate $LaL_2(NO_3)_3$ (3a)

Using the general procedure from 0.22 g (0.5 mmol) **2a** and 0.46 g (1.25 mmol) **1** in 1 mL ethanol, which was then evaporated, diethyl ether (2 mL) was added to the resulting oil, and after 60 min, a white crystalline precipitate was formed. After additional cooling at –4°C, 0.42 g (79%) **3a** was obtained with a melting range of 108–121°C. The product was dissolved in ethanol under gentle heating, and 8 mL diethyl ether was added. After cooling the solution at –4°C overnight, the resulting product has a melting range of 110–117°C. Found: C, 20.12; H, 4.29; N, 4.13. $C_{18}H_{42}Br_2LaN_3O_{21}P_4$ (1059.142) requires C, 20.41; H, 4.00; N, 3.97. IR: ν_{max}(nujol),cm^{-1}: 1020–1040 (P-O-C), 1219 (P=O), 1320 (N-O). $\nu_{max}(CHCl_3)$,cm^{-1}: 1030 (P-O-C), 1225 (P=O), 1315 (N-O), 1455 (N=O). ^{1}H-NMR δ_H (ppm, $CDCl_3$): 1.42 [6H, t, ^3J(HH) 8.23 Hz,C$\underline{H}_3$CH$_2$O], 1.41 [6H, t, ^3J(HH) 6.41 Hz, C$\underline{H}_3$CH$_2$O], 4.15–4.31 [4H, m, CH$_3$C$\underline{H}_2$O], 4.31–4.41 [4H, m, CH$_3$C$\underline{H}_2$O], 4.41 [1H, t, ^2J(PH) 19.40 Hz, P$_2$C$\underline{H}$Br]. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ_C: 16.0–16.2 [m, $\underline{C}$H$_3$CH$_2$O], 24.1 [t, ^1J(CP) 140.3 Hz, P$_2\underline{C}$HBr], 65.7–65.9 [m, CH$_3\underline{C}$H$_2$O], 66.2–66.4 [m, CH$_3\underline{C}$H$_2$O].

Tetraethyl Ester of Bromomethylenediphosphonic Acid Cerium(III) Nitrate $CeL_2(NO_3)_3$ (3b)

Mixing 0.43 g (1.0 mmol) **2b** and 0.92 g (2.5 mmol) **1** in ethanol (2 mL) for 60 min gave an oil. After adding diethyl ether (4 mL), a white precipitate formed. The mixture was cooled at –4°C, and 0.90 g (85%) **3b** was obtained with melting range of 104–117°C. The product was recrystallized by dissolving it in ethanol at heating, and diethyl ether (4 mL) was added. After cooling the solution overnight at –4°C, the resulting product had a melting range of 108–121°C. Found: C, 20.70; H, 3.96; N, 4.12. $C_{18}H_{42}Br_2CeN_3O_{21}P_4$ (1060.353) requires C, 20.39; H, 3.99; N, 3.96. ν_{max}(nujol),cm^{-1}: 1020–1035 (P-O-C), 1220 (P=O), 1320 (N-O). $\nu_{max}(CHCl_3)$,cm^{-1}: 1035 (P-O-C), 1225 (P=O), 1315 (N-O),

1460 (N=O). ^{1}H-NMR δ_H (ppm, $CDCl_3$): 1.19 [6H, t, ^3J(HH) 6.65 Hz, $C\underline{H_3}CH_2O$], 2.01 [6H, t, ^3J(HH) 5.82 Hz, $C\underline{H_3}CHO$], 4.06–4.37 [4H, m, $CH_3C\underline{H_2}O$], 5.66–5.99 [4H, m, $CH_3C\underline{H_2}O$;], 8.24 [1H, t, ^2J(HP) 16.28 Hz, $P_2C\underline{H}Br$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ_C: 15.9–16.1 [m, $\underline{C}H_3CH_2O$], 16.9–17.0 [m, $\underline{C}H_3CH_2O$], 26.4 [t, ^1J(CP) 140.3 Hz, $P_2\underline{C}HBr$], 66.1–66.3 [m,$CH_3\underline{C}H_2O$], 67.8–68.1 [m, $CH_3\underline{C}H_2O$].

Tetraethyl Ester of Bromomethylenediphosphonic Acid Samarium(III) Nitrate $SmL_2(NO_3)_3$ (3c)

Mixing 0.22 g (0.5 mmol) **2c** and 0.46 g (1.25 mmol) **1** in ethanol (1 mL) for 60 min gave oily crystals. After washing the crystals with diethyl ether (2 mL) and cooling the mixture overnight, 0.36 g (67%) **3c** was obtained with melting range of 94–99°C. The product was dissolved in ethanol under gentle heating, and a mixture of diethyl ether (2.5 mL) and hexane (0.2 mL) was added. After cooling, white crystals were formed with a melting range of 94–100°C. Found: C, 20.41; H, 3.83; N, 4.11. $C_{18}H_{42}Br_2N_3O_{21}P_4Sm$ (1070.597) requires C, 20.19; H, 3.95; N, 3.92. ν_{max}(nujol),cm^{-1}: 1010–1030 (P-O-C), 1210 (P=O), 1310 (N-O). ν_{max}($CHCl_3$),cm^{-1}: 1025 (P-O-C), 1215 (P=O), 1300 (N-O), 1465 (N=O). ^{1}H NMR δ_H (ppm, $CDCl_3$): 1.35 [6H, t, ^3J(HH) 7.02 Hz, $C\underline{H_3}CH_2O$], 1.48 [6H, t, ^3J(HH) 7.03 Hz, $C\underline{H_3}CH_2O$], 4.35–4.11 [4H, m, $CH_3C\underline{H_2}O$], 4.65–4.47 [4H, m, $CH_3C\underline{H_2}O$], 4.83 [1H, t, ^2J(HP) 19.61 Hz, $P_2C\underline{H}Br$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ_C: 16.1 [pseudo-t, ^3J(CP) 2.5 Hz, $\underline{C}H_3CH_2OP$], 16.2 [pseudo-t, ^3J(CP) 3.0 Hz, $\underline{C}H_3CH_2OP$], 25.0 [t, ^1J(CP) 140.9 Hz, $P_2\underline{C}HBr$], 66.0 [pseudo-t, ^2J(CP) 2.3 Hz, $CH_3\underline{C}H_2OP$], 66.5 [pseudo-t, ^2J(CP) 3.3 Hz, $CH_3\underline{C}H_2OP$].

Tetraethyl Ester of Bromomethylenediphosphonic Acid Gadolinium(III) Nitrate $GdL_2(NO_3)_3$ (3d)

Mixing 0.22 g (0.5 mmol) **2d** and 0.39 g (1.05 mmol) **1** in ethanol (1 mL) for 60 min gave an oil. After adding diethyl ether (2 mL) and stirring for 1 h, white crystals formed: 0.37 g (69%) **3d** with melting range of 80–83°C. After dissolving in ethanol under heating, adding diethyl ether (2 mL) and hexane (0.1 mL), and cooling the mixture, the isolated product had a melting range of 76–84°C. Found C, 19.99; H, 4.04; N, 3.91. $C_{18}H_{42}Br_2GdN_3O_{21}P_4$ (1077.487) requires C, 20.06; H, 3.93; N, 3.90. ν_{max}(nujol),cm^{-1}: 1010–1030 (P-O-C), 1210 (P=O), 1310 (N-O). ν_{max}($CHCl_3$),cm^{-1}: 1030 (P-O-C), 1220 (P=O), 1305 (N-O), 1470 (N=O). EPR (ν = 9.748 GHz): H_i = 3529 G. $g_i = 1.974 \pm 0.0002$.

Tetraethyl Ester of Bromomethylenediphosphonic Acid Erbium(III) Nitrate $Er_2L_3(NO_3)_6$ (3e)

Mixing 0.22 g (0.5 mmol) **2e** and 0.39 g (1.05 mmol) **1** in ethanol (1 mL) for 60 min gave an oil. Diethyl ether (2 mL) was added and mixture was stirred for 1 h to give 0.34 g (75%) **3e** with a melting range of 134–141°C. The obtained pink crystals were dissolved in ethanol under gentle heating, and diethyl ether (1 mL) was added. After cooling the solution at 4°C, a precipitate was obtained with a melting range of 142–148°C. Found: C, 17.79; H, 3.75; N, 5.04. $C_{27}H_{63}Br_3Er_2N_6O_{36}P_6$ (1807.880) requires C, 17.94; H, 3.51; N, 4.64. ν_{max}(nujol),cm^{-1}: 1020–1050 (P-O-C), 1220 (P=O), 1330 (N-O). ν_{max}($CHCl_3$),cm^{-1}: 1030 (P-O-C), 1220 (P=O), 1313 (N-O), 1482 (N=O).

Tetraethyl Ester of Bromomethylenediphosphonic Acid Ytterbium(III) Nitrate $Yb_2L_3(NO_3)_6$ (3f)

Mixing 0.22 g (0.5 mmol) **2f** and 0.39 g (1.05 mmol) **1** in ethanol (1 mL) for 60 min gave an oil. After adding diethyl ether (2 mL) and cooling the mixture for 12 h, a white crystalline precipitate was formed: 0.34 g (75%) **3f** with a melting range 133–141°C. The product was dissolved in ethanol under heating, and diethyl ether (2.5 mL) was added. After cooling overnight, the resulting crystalline product was obtained with a melting range 141–147°C. Found: C, 17.84; H, 3.60; N, 5.00. $C_{27}H_{63}Br_3N_6O_{36}P_6Yb_2$ (1819.442) requires C, 17.82; H, 3.49; N, 4.62. ν_{max}(nujol),cm^{-1}: 1020–1030 (P-O-C), 1205 (P=O), 1310 (N-O). ν_{max}($CHCl_3$),cm^{-1}: 1025 (P-O-C), 1210 (P=O), 1300 (N-O), 1485 (N=O).

Tetraisopropyl Ester of Bromomethylenediphosphonic Acid Lanthanum(III) Nitrate $LaL_2(NO_3)_3$ (5a)

Mixing 0.22 g (0.5 mmol) **2a** and 0.53 g (1.25 mmol) **4** in ethanol (1 mL) for 60 min gave an oil. The product was obtained after adding diethyl ether (2 mL) and hexane (3 mL) and cooling the mixture overnight. White crystals were obtained: 0.27 g (46%) **5a**, melting range 146–152°C. Found: C, 27.09; H, 5.02; N, 3.66. $C_{26}H_{58}Br_2LaN_3O_{21}P_4$ (1171.355) requires C, 26.66; H, 4.99; N, 3.59. ν_{max}(nujol),cm^{-1}: 980–1010 (P-O-C), 1215 (P=O), 1295 (N-O). ^{1}H-NMR δ_H (ppm, $CDCl_3$): 1.39 [6H, d, ^3J(HH) 6.06 Hz, ($C\underline{H}_3$)$_2$CHO], 1.41 [12H, d, ^3J(HH) 6.14 Hz, ($C\underline{H}_3$)$_2$CHO], 1.45 [6H, d, ^3J(HH) 6.22, ($C\underline{H}_3$)$_2$CHO], 4.32 [1H, t, ^2J(HP) 19.76 Hz, $P_2C\underline{H}Br$], 4.83 [2H, d sp, ^3J(HP) 6.25 Hz, ^3J(HH) 6.25 Hz, $(CH_3)_2C\underline{H}OP$], 4.94 [2H, d sp, ^3J(HP) 6.23 Hz, ^3J(HH) 6.23 Hz, $(CH_3)_2C\underline{H}OP$]. ^{13}C{^{1}H}-NMR ($CDCl_3$) δ_C: 23.5 [pseudo t, ^3J(CP) 2.9 Hz, ($\underline{C}H_3$)$_2$CHO], 23.6 [pseudo t, ^3J(CP) 3.4 Hz, ($\underline{C}H_3$)$_2$CHO], 23.7 [pseudo t, ^3J(CP) 1.1 Hz, ($\underline{C}H_3$)$_2$CHO], 23.8 [pseudo t, ^3J(CP) 1.4 Hz,

($\underline{C}H_3)_2CHO$], 25.3 [t, ^1J(CP) 140.4 Hz, $P_2\underline{C}HBr$], 75.4 [pseudo t, ^2J(CP) 2.9 Hz, $(CH_3)_2\underline{C}HO$], 75.8 [pseudo t, ^2J(CP) 3.6 Hz, $(CH_3)_2\underline{C}HO$].

Tetraisopropyl Ester of Bromomethylenediphosphonic Adic Cerium(III) Nitrate $CeL_2(NO_3)_3$ (5b)

Mixing 0.22 g (0.5 mmol) **2b** and 0.53 g (1.25 mmol) **4** in 1 mL ethanol for 60 min gave a white crystalline precipitate. After cooling the mixture, the product was filtered and gave 0.26 g (44%) **5b**, with a melting range of 144–154°C. The product was dissolved in ethanol under heating (50°C), a mixture of diethyl ether (2 mL) and hexane (0.75 mL) was added. After cooling at 5°C, the product was obtained with a melting range of 150–156°C. Found: C, 26.75; H, 4.87; N, 3.58. $C_{26}H_{58}Br_2CeN_3O_{21}P_4$ (1172.565) requires C, 26.63; H, 4.99; N, 3.58. ν_{max}(nujol),cm^{-1}: 970–1010 (P-O-C), 1210 (P=O), 1295 (N-O). ^{1}H-NMR δ_H (ppm, $CDCl_3$): 0.78 [6H, d, ^3J(HH) 5.53 Hz, $(C\underline{H}_3)_2CHO$], 1.25 [6H, d, ^3J(HH) 5.62 Hz, $(C\underline{H}_3)_2CHO$], 1.85 [6H, d, ^3J(HH) 5.72 Hz, $(C\underline{H}_3)_2CHO$], 2.19 [6H, d, ^{3}J(HH) 5.70 Hz, $(C\underline{H}_3)_2CHO$], 4.87–4.69 [2H, m, $(CH_3)_2C\underline{H}O$], 6.99–7.15 [2H, m, $(CH_3)_2C\underline{H}O$], 9.80 [1H, t, ^2J(HP) 19.57 Hz, $P_2C\underline{H}Br$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ_C: 23.5–23.7 [m, $(\underline{C}H_3)_2CHO$], 24.5–24.7 [m, $(\underline{C}H_3)_2CHO$], 24.7–24.8 [m, $(\underline{C}H_3)_2CHO$], 29.9 [t, ^1J(CP) 140.7 Hz, $P_2\underline{C}HBr$], 75.9–76.1 [m, $(CH_3)_2\underline{C}HO$], 77.9–78.1 [m, $(CH_3)_2\underline{C}HO$].

Tetraisopropyl Ester of Bromomethylenediphosphonic Acid Samarium(III) Nitrate $SmL_2(NO_3)_3$ (5c)

After mixing 0.22 g (0.5 mmol) **2c** and 0.53 g (1.25 mmol) **4** in ethanol (1 mL) for 60 min and cooling, a white crystalline precipitate was formed: 0.29 g (49%) **5c** with a melting range of 145–150°C. Found: C, 26.41; H, 4.88; N, 3.56. $C_{26}H_{58}Br_2N_3O_{21}P_4Sm$ (1182.809) requires C, 26.40; H, 4.94; N, 3.55. ν_{max}(nujol),cm^{-1}: 990–1010 (P-O-C), 1217 (P=O), 1300 (N-O). ^{1}H NMR δ_H (ppm, $CDCl_3$): 1.32 [6H, d, ^3J(HH) 6.04 Hz, $(C\underline{H}_3)_2CHO$], 1.35 [6H, d, ^3J(HH) 6.11 Hz, $(C\underline{H}_3)_2CHO$], 1.48 [6H, d, ^3J(HH) 6.08 Hz, $(C\underline{H}_3)_2CHO$], 1.56 [6H, d, ^3J(HH) 6.13 Hz, $(C\underline{H}_3)_2CHO$], 4.84–4.70 [2H, m, $(CH_3)_2C\underline{H}O$], 4.93 [1H, t, ^2J(HP) 19.93 Hz, $P_2C\underline{H}Br$], 5.43–5.20 [2H, m, $(CH_3)_2C\underline{H}O$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ_C: 23.4–23.6 [m, $(\underline{C}H_3)_2CHO$], 23.8–23.9 [m, $(\underline{C}H_3)_2CHO$], 23.9–24.0 [m, $(\underline{C}H_3)_2CHO$], 26.4 [t, ^1J(CP) 139.8 Hz, $P_2\underline{C}HBr$], 75.5–75.6 [m, $(CH_3)_2\underline{C}HO$], 76.2–76.3 [m, $(CH_3)_2\underline{C}HO$].

Tetraisopropyl Ester of Bromomethylenediphosphonic Acid Gadolinium(III) Nitrate $GdL_2(NO_3)_3$ (5d)

0.22 g (0.5 mmol) **2d** and 0.44 g (1.05 mmol) **4** in ethanol (1 mL) were mixed for 60 min. After evaporation of the solvent and adding hexane (2 mL) and diethyl ether (0.5 mL), a white crystalline product was isolated: 0.48 g (81%) **5d** with a melting range of 120–137°C. The crystals were dissolved in ethanol at 50°C, and after the addition of diethyl ether (0.5 mL) and hexane (1 mL), the product was obtained with a melting range of 139–142°C. Found: C, 26.26; H, 4.96; N, 3.53. $C_{26}H_{58}Br_2GdN_3O_{21}P_4$ (1189.699) requires C, 26.25; H, 4.91; N, 3.53. ν_{max}(nujol),cm^{-1}: 990–1015 (P-O-C), 1225 (P=O), 1310 (N-O). EPR (ν = 9.748 GHz): H_i = 3504 G, $g_i = 1.988 \pm 0.0002$.

Tetraisopropyl Ester of Bromomethylenediphosphonic Acid Erbium(III) Nitrate $Er_2L_3(NO_3)_6$ (5e)

Mixing 0.22 g (0.5 mmol) **2e** and 0.44 g (1.05 mmol) **4** in ethanol (1 mL) for 60 min and evaporation of the solvent gave an oil. The oil was washed with diethyl ether:hexane 4:1 two times and then with diethyl ether, after which crystalline precipitate was obtained: 0.16 g (32%) **5e,** melting range of 125–131°C. Found: C, 23.80; H, 4.52; N, 4.25. $C_{39}H_{87}Br_3Er_2N_6O_{36}P_6$ (1976.199) requires C, 23.70; H, 4.44; N, 4.25. ν_{max}(nujol),cm^{-1}: 1000–1030 (P-O-C), 1205 (P=O), 1305 (N-O).

Tetraisopropyl Ester of Bromomethylenediphosphonic Acid Ytterbium(III) Nitrate $Yb_2L_3(NO_3)_6$ (5f)

Mixing 0.22 g (0.5 mmol) **2f** and 0.44 g (1.05 mmol) **4** in ethanol (1 mL) for 60 min and evaporating the solvent gave an oil. The oil was dispersed in a hexane:diethyl ether mixture 4:1 and cooled. The resulting crystal precipitate was filtered and gave 0.40 g (80%) **5f** with a melting range of 100–120°C. The product was washed with a mixture of diethyl ether:hexane 1:5, and the melting range became 120–130°C. Found: C, 23.46; H, 4.20; N, 4.22. $C_{39}H_{87}Br_3N_6O_{36}P_6Yb_2$ (1987.761) requires C, 23.57; H, 4.41; N, 4.23. ν_{max}(nujol),cm^{-1}: 980–1020 (P-O-C), 1205 (P=O), 1300 (N-O).

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