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Syntheses, spectroscopic study and X-ray crystallography of some new phosphoramidates and lanthanide(III) complexes of *N*-(4-nitrobenzoyl)-*N'*,*N''*-bis(morpholino)phosphoric triamide

New phosphoramidates with the formula $RC(O)N(H)P(O)X_2$, $R = 2\text{-NO}_2\text{-C}_6\text{H}_4$, $3\text{-NO}_2\text{-C}_6\text{H}_4$ and $4\text{-NO}_2\text{-C}_6\text{H}_4$, $X = N(\text{CH}_2\text{CH}_3)$ (1)–(3), NC_4H_8 (4)–(6), and $\text{NC}_4\text{H}_8\text{O}$ (7)–(9) were synthesized and characterized by ^1H , ^{13}C , ^{31}P NMR and IR spectroscopy, and elemental analysis. The reaction of (9) with hydrated lanthanide(III) nitrate leads to ten- or nine-coordinated complexes, (10)–(13). The crystal structure has been determined for (3), (5), (9), (10) and (13). In contrast to all of the previously reported similar phosphoramidate compounds, the $-\text{C}(\text{O})-\text{N}(\text{H})-\text{P}(\text{O})$ skeleton in the free ligand (9) shows a *cisoid* conformation, with the $\text{C}=\text{O}$ and $\text{P}=\text{O}$ double bonds adopting a nearly *syn* conformation. Quantum chemical calculations were applied for clarifying this exceptional conformational behavior. The monodentate neutral ligand (9) is coordinated to the metal ions *via* the phosphoryl O atom, adopting the usual *anti* conformation between the $\text{C}=\text{O}$ and $\text{P}=\text{O}$ groups.

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1. Introduction

The chemistry of phosphoramidates has been developed recently due to their biological activity (Baldwin *et al.*, 2003; Pang *et al.*, 2003), their coordination chemistry (Gubina, Ovchinnikov *et al.*, 2000; Trush *et al.*, 1999; Amirkhanov, Ovchinnikov *et al.*, 1997; Amirkhanov, Ovchinnikov *et al.*, 1997) and the catalytic behavior of these compounds (Denmark & Fu, 2003; Denmark *et al.*, 2006). Recently, novel synthesized phosphoramidate from 3-hydroxypropyl derivatives of nonsteroidal anti-inflammatory drugs (NSAID) showed significantly greater inhibitory activity than the corresponding 3-hydroxypropyl derivatives (Wittine *et al.*, 2009). Moreover, amino acid phosphoramidate nucleotides were reported as alternative substrates for HIV-1 reverse transcriptase (Adelfinskaya & Herdewijn, 2007). Phosphoramidates of the general formula $RC(O)NHP(O)X_2$, are P,N-substituted analogues of β -diketones and are potential *O,O'*-donor ligands. The first studies of the coordination chemistry of phosphoramidates were devoted to complexes of the lanthanides because of the high affinity of the phosphoryl group for the rare-earth elements (Caudle *et al.*, 1985). Although the crystal structures of some phosphoramidates and a few complexes have been reported recently (Gholivand, Mostaanzadeh *et al.*, 2006; Skopenko *et al.*, 2004), little is known about high coordination number complexes of lanthanide with monodentate phosphoramidate ligands (Ovchinnikov *et al.*, 2000). Very recently, Znovjyak *et al.* (2009) reported the syntheses and magnetic properties of lanthanide complexes with phosphoramidates and 1,10-

phenanthroline ligands. Moreover, the crystal structures of neodymium complexes were determined.

In this work we report on the synthesis, the spectroscopic characterization, elemental and thermal analysis, and the X-ray crystal structure determination of several new phosphoramidates with the general formula $n\text{-NO}_2\text{-C}_6\text{H}_4\text{C(O)NHP(O)X}_2$ (1)–(9), with $n = 1\text{--}3$ and $X =$ amine (diethyl amine, pyrrolidine and morpholine). Furthermore, the utility of these compounds as ligands for coordination chemistry with lanthanide metals was evaluated. The synthesis and spectroscopic characterization of four lanthanide(III) metal complexes (10)–(13) with the N -(4-nitrobenzoyl)- N' , N'' -bis(morpholino) phosphoric triamide ligand are reported, including the determination of the crystal structure for (10) (La^{3+}) and (13) (Er^{3+}).

2. Experimental

2.1. Spectroscopic measurements

^1H , ^{13}C and ^{31}P spectra were recorded on a Bruker Avance DRS 500 spectrometer. ^1H and ^{13}C chemical shifts were determined relative to internal TMS, ^{31}P chemical shifts relative to 85% H_3PO_4 as an external standard. Table 1 lists the most relevant NMR data for the compounds studied. IR spectra were recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus. Melting points were obtained with an Electrothermal instrument. Differential thermal analysis (DTA) and thermal gravitational analysis (TGA) were performed on a Perkin–Elmer Pyris Diamond TG/DTA thermal analyses system performed in nitrogen with a heating rate of 10 K min^{-1} from 313 to 973 K. $n\text{-NO}_2\text{-C}_6\text{H}_4\text{C(O)NHP(O)Cl}_2$ ($n = 2, 3$ and 4) were prepared by a procedure similar to that by Kirsanov & Makitra (1956) from the reaction of phosphorus pentachloride with n -nitrobenzamide ($n = 2, 3$ and 4) and then treatment with formic acid.

2.2. X-ray measurements

X-ray data of (5) were collected on a four-cycle diffractometer Gemini equipped with an Atlas CCD detector, for (3), (9) and (10) on a Bruker SMART 1000 CCD area detector, and for (13) data were collected on a Stoe Mark II image-plate diffraction system equipped with a two-circle goniometer. In all cases graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) was used. All the structures were solved by direct methods. Structure (5) was refined with *JANA2006* (Petricek *et al.*, 2006), and structures (3), (9), (10) and (13) with *SHELXL97* (Sheldrick, 2008), using the full-matrix least-squares method. *JANA2006* uses the weighting scheme based on the experimental expectations (see *_refine_ls_weighting_details* in the CIF) that do not force S to be one. Therefore, the values of S are usually larger than those from the *SHELX* program (see Table 2). In (9) one of two morpholine moieties is disordered by two positions with relative occupancies equal to 0.55:0.45. Atoms N2 and C5A are common to both disordered parts. Owing to the close positions of the

disordered atoms all distances inside the ring were restrained with *DFIX* instructions, and an ADP instruction was applied to make ADPs of chemically equivalent atoms equal. CCDC 709114, 691914, 678070, 678074 and 713519 contain the supplementary crystallographic data for (3), (5), (9), (10) and (13), respectively. X-ray powder diffraction (XRD) measurements have been performed using a Philips diffractometer of X'pert Company with monochromated $\text{Cu K}\alpha$ radiation. The *ORTEP* program was used for making the stereo drawings (Farrugia, 1997).

2.3. Quantum chemical calculations

Full geometry optimization and frequency calculations were performed using the program package *GAUSSIAN03* by applying the DFT/B3LYP methods using the 6-31+G* basis set (Frisch *et al.*, 2003). The calculated vibrational properties corresponded in all cases to potential energy minima for which no imaginary frequency was found.

2.3.1. General procedure for the synthesis of (1)–(9). To a stirred solution of 2-nitrobenzoyl, 3-nitrobenzoyl and 4-nitrobenzoyl phosphoramidic dichloride in dry acetonitrile (20 ml), a solution of corresponding amine (diethyl amine, pyrrolidine or morpholine) was added dropwise at 268 K. After 8 h stirring, the product was filtered off and then washed with distilled water.

2.3.2. General procedure for the synthesis of (10)–(13). $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ of commercial grade was used without further purification. HC(OEt)_3 (0.5 ml, 3 mmol) was added to a boiling solution of 0.5 mmol of lanthanide(III) nitrate in 7 ml of dry acetone. A solution of 0.384 g (1 mmol) of $4\text{-NO}_2\text{-C}_6\text{H}_4\text{C(O)N(H)P(O)(NC}_4\text{H}_8\text{O)}_2$ (9) in 10 ml of dry methanol was added. The solution was allowed to stand in a vacuum desiccator over CaCl_2 . After 2 d monocrystals of (10) and (13) were precipitated, washed with cold chloroform and acetone, and dried in air. The complexes are stable in air, insoluble in common polar and nonpolar organic solvents.

2.3.3. N -(2-Nitrobenzoyl)- N' , N'' , N''' -tetraethyl phosphoric triamide (1). Yield: 65%, m.p. 414 K. ^1H NMR (500.13 MHz, CDCl_3): $\delta = 1.09$ [t, $^3J(\text{H,H}) = 7.1\text{ Hz}$, 12H, CH_3], 3.13 (m, 8H, CH_2), 7.54 (m, 2H, Ar-H), 7.63 [t, $^3J(\text{H,H}) = 7.4\text{ Hz}$, 1 H, Ar-H], 8.03 [d, $^3J(\text{H,H}) = 8.3\text{ Hz}$, 1 H, Ar-H], 9.20 (br, 1H, NH). ^{13}C NMR (125.76 MHz, CDCl_3) $\delta = 13.98$ [d, $^3J(\text{P,C}) = 2.7\text{ Hz}$], 39.38 [d, $^2J(\text{P,C}) = 5.2\text{ Hz}$], 124.22 (s), 128.57 (s), 130.18 (s), 133.16 (s), 133.35 [d, $^3J(\text{P,C}) = 9.3\text{ Hz}$], 146.57 (s), 167.39 (s). ^{31}P NMR (202.46 MHz, CDCl_3): $\delta = 14.26$ (s) p.p.m. IR (KBr, cm^{-1}): 3030 ($\nu\text{N-H}$), 2855, 1674 ($\nu\text{C=O}$), 1525, 1452, 1211 ($\nu\text{P=O}$), 1178 ($\nu\text{P=O}$), 1027, 851 ($\nu\text{P-N}$), 820 ($\nu\text{P-N}$), 727 ($\nu\text{P-N}$). Anal.: calc. for $\text{C}_{15}\text{H}_{25}\text{N}_4\text{O}_4\text{P}$: C 50.6, H 7.0, N 15.7%; found: C 50.4, H 7.3, N 15.9%.

2.3.4. N -(3-Nitrobenzoyl)- N' , N'' , N''' -tetraethyl phosphoric triamide (2). Yield: 47%, m.p. 376 K. ^1H NMR (500.13 MHz, CDCl_3): $\delta = 1.11$ [t, $^3J(\text{H,H}) = 7.1\text{ Hz}$, 12H, CH_3], 3.13 [m, $^3J(\text{H,H}) = 7.1\text{ Hz}$, 8H, CH_2], 7.61 [t, $^3J(\text{H,H}) = 7.9\text{ Hz}$, 1H, Ar-H], 8.35 [dt, $^3J(\text{H,H}) = 8.0\text{ Hz}$, $^5J(\text{H,H}) = 1.1\text{ Hz}$, 1 H, Ar-H], 8.57 [d, $^3J(\text{H,H}) = 8.0\text{ Hz}$, 1H, Ar-H], 9.17 (s, 1H, Ar-H) 10.31 (br, 1H, NH). ^{13}C NMR (125.76 MHz, CDCl_3): $\delta = 13.86$

[d, $^3J(\text{P,C}) = 2.7 \text{ Hz}$], 39.46 [d, $^2J(\text{P,C}) = 5.2 \text{ Hz}$], 123.90 (s), 126.32 (s), 129.18 (s), 134.49 (s), 135.84 [d, $^3J(\text{P,C}) = 9.5 \text{ Hz}$], 148.43 (s), 166.27 (s). ^{31}P NMR (202.46 MHz, CDCl_3): $\delta = 15.43$ (m) p.p.m. IR (KBr, cm^{-1}): 3030 ($\nu\text{N-H}$), 2855, 1670 ($\nu\text{C=O}$), 1523, 1444, 1209 ($\nu\text{P=O}$), 1178 ($\nu\text{P=O}$), 1018, 849 ($\nu\text{P-N}$), 809 ($\nu\text{P-N}$), 716 ($\nu\text{P-N}$). Anal.: calc. for $\text{C}_{15}\text{H}_{25}\text{N}_4\text{O}_4\text{P}$: C 50.6, H 7.0, N 15.7%; found: C 50.7, H 7.2, N 15.4%.

2.3.5. *N*-(4-Nitrobenzoyl)-*N'*,*N''*,*N'''*-tetraethyl phosphoric triamide (3). Yield: 74%, m.p. 462 K. ^1H NMR (500.13 MHz, CDCl_3): $\delta = 1.12$ [t, $^3J(\text{H,H}) = 6.9 \text{ Hz}$, 12H, CH_3], 3.19 [m, $^3J(\text{H,H}) = 6.9 \text{ Hz}$, 8H, CH_2], 8.25 [d, $^3J(\text{H,H}) = 7.2 \text{ Hz}$, 2H, Ar-H], 8.38 [d, $^3J(\text{H,H}) = 7.2 \text{ Hz}$, 2H, Ar-H], 10.05 (s, 1H, NH). ^{13}C NMR (125.76 MHz, CDCl_3): $\delta = 13.95$ [d, $^3J(\text{P,C}) = 2.4 \text{ Hz}$], 39.55 [d, $^2J(\text{P,C}) = 5.2 \text{ Hz}$], 123.30 (s), 129.76 (s), 139.43 [d, $^3J(\text{P,C}) = 9.2 \text{ Hz}$], 149.90 (s), 166.50 (s). ^{31}P NMR (202.46 MHz, CDCl_3): $\delta = 15.47$ (m). IR (KBr, cm^{-1}): 3040 ($\nu\text{N-H}$), 2860, 1663 ($\nu\text{C=O}$), 1516, 1433, 1212 ($\nu\text{P=O}$), 1180, 1023, 838 ($\nu\text{P-N}$), 816 ($\nu\text{P-N}$), 718 ($\nu\text{P-N}$). Anal.: calc. for $\text{C}_{15}\text{H}_{25}\text{N}_4\text{O}_4\text{P}$: C 50.6, H 7.0, N 15.7%; found: C 50.3, H 7.3, N 15.5%.

2.3.6. *N*-(2-Nitrobenzoyl)-*N'*,*N''*-bis(pyrolidino)phosphoric triamide (4). Yield: 52%, m.p. 454 K. ^1H NMR (500.13 MHz, CDCl_3): $\delta = 1.83$ (m, 8H, CH_2), 3.23 (m, 4H, CH_2), 3.32 (m, 4H, CH_2), 7.56 (m, 2H, Ar-H), 7.66 [dt, $^3J(\text{H,H}) = 7.5 \text{ Hz}$, $^4J(\text{H,H}) = 1.1 \text{ Hz}$, 1H, Ar-H], 8.03 [dd, $^3J(\text{H,H}) = 8.1 \text{ Hz}$, $^4J(\text{H,H}) = 1.0 \text{ Hz}$, 1H, Ar-H], 8.58 (s, 1H, NH). ^{13}C NMR (125.76 MHz, CDCl_3): $\delta = 26.33$ [d, $^3J(\text{P,C}) = 8.3 \text{ Hz}$], 46.28 [d, $^2J(\text{P,C}) = 5.2 \text{ Hz}$], 124.36 (s), 128.49 (s), 130.48 (s), 133.09 [d, $^3J(\text{P,C}) = 8.9 \text{ Hz}$], 133.37 (s), 146.59 (s), 167.43 [d, $^2J(\text{P,C}) = 3.1 \text{ Hz}$, C=O]. ^{31}P NMR (202.46 MHz, CDCl_3): $\delta = 8.69$ (s). IR (KBr, cm^{-1}): 3040 ($\nu\text{N-H}$), 2935, 1680 ($\nu\text{C=O}$), 1521, 1447, 1209 ($\nu\text{P=O}$), 1177, 1088, 1013, 857 ($\nu\text{P-N}$), 823 ($\nu\text{P-N}$), 728 ($\nu\text{P-N}$). Anal.: calc. for $\text{C}_{15}\text{H}_{21}\text{N}_4\text{O}_4\text{P}$: C 51.1, H 6.0, N 15.9%; found: C 50.9, H 6.3, N 15.6%.

2.3.7. *N*-(3-Nitrobenzoyl)-*N'*,*N''*-bis(pyrolidino)phosphoric triamide (5). Yield: 83%, m.p. 457 K. ^1H NMR (500.13 MHz, CDCl_3): $\delta = 1.82$ (m, 8H), 3.24 (m, 4H, CH_2), 3.39 (m, 4H, CH_2), 7.62 [t, $^3J(\text{H,H}) = 8.0 \text{ Hz}$, 1H, Ar-H], 8.36 [dm, $^3J(\text{H,H}) = 8.2 \text{ Hz}$, $^4J(\text{H,H}) = 1.0 \text{ Hz}$, 1H, Ar-H], 8.54 [dt, $^3J(\text{H,H}) = 7.8 \text{ Hz}$, $^5J(\text{P,H}) = 1.3 \text{ Hz}$, 1H, Ar-H], 9.24 [t, $^5J(\text{P,H}) = 1.8 \text{ Hz}$, 1H, Ar-H], 10.25 (s, 1H, NH). ^{13}C NMR (125.76 MHz, CDCl_3): $\delta = 26.36$ [d, $^3J(\text{P,C}) = 8.3 \text{ Hz}$], 46.37 [d, $^2J(\text{P,C}) = 5.4 \text{ Hz}$], 123.90 (s), 126.43 (s), 129.27 (s), 134.55 (s), 135.62 [d, $^3J(\text{P,C}) = 9.2 \text{ Hz}$], 148.47 (s), 166.15 [d, $^2J(\text{P,C}) = 2.0 \text{ Hz}$, C=O]. ^{31}P NMR (202.45 MHz, CDCl_3): $\delta = 9.79$ (m). IR (KBr, cm^{-1}): 3080 ($\nu\text{N-H}$), 2935, 1669 ($\nu\text{C=O}$), 1520, 1434, 1346, 1210 ($\nu\text{P=O}$), 1178 ($\nu\text{P=O}$), 1079, 850 ($\nu\text{P-N}$), 818 ($\nu\text{P-N}$), 703 ($\nu\text{P-N}$). Anal.: calc. for $\text{C}_{15}\text{H}_{21}\text{N}_4\text{O}_4\text{P}$: C 51.1, H 6.0, N 15.9%; found: C 51.3, H 6.1, N 16.1%.

2.3.8. *N*-(4-Nitrobenzoyl)-*N'*,*N''*-bis(pyrolidino)phosphoric triamide (6). Yield: 87%, m.p. 497 K. ^1H NMR (500.13 MHz, CDCl_3): $\delta = 1.83$ (m, 8H, CH_2), 3.22 (m, 4H, CH_2), 3.37 (m, 4H, CH_2), 8.25 [d, $^3J(\text{H,H}) = 8.8 \text{ Hz}$, 2H, Ar-H], 8.37 [d, $^3J(\text{H,H}) = 8.8 \text{ Hz}$, 2H, Ar-H], 8.58 (s, 1H, NH). ^{13}C NMR (125.76 MHz, CDCl_3): $\delta = 26.35$ [d, $^3J(\text{P,C}) = 8.3 \text{ Hz}$], 46.41 [d, $^2J(\text{P,C}) = 5.3 \text{ Hz}$], 123.36 (s), 129.79 (s), 139.20 [d,

$^3J(\text{P,C}) = 8.8 \text{ Hz}$], 149.95 (s), 166.45 [d, $^2J(\text{P,C}) = 2.0 \text{ Hz}$, C=O]. ^{31}P NMR (202.46 MHz, CDCl_3): $\delta = 9.88$ (s). IR (KBr, cm^{-1}): 3060 ($\nu\text{N-H}$), 2935, 1672 ($\nu\text{C=O}$), 1513, 1448, 1209 ($\nu\text{P=O}$), 1178, 1075, 1010, 874 ($\nu\text{P-N}$), 840 ($\nu\text{P-N}$), 711 ($\nu\text{P-N}$). Anal.: calc. for $\text{C}_{15}\text{H}_{21}\text{N}_4\text{O}_4\text{P}$: C 51.1, H 6.0, N 15.9%; found: C 51.4, H 5.8, N 15.7%.

2.3.9. *N*-(2-Nitrobenzoyl)-*N'*,*N''*-bis(morpholino)phosphoric triamide (7). Yield: 58%, m.p. 526 K. ^1H NMR (500.13 MHz, CDCl_3): $\delta = 3.19$ (m, 8H, CH_2), 3.62 [t, $^3J(\text{H,H}) = 4.4 \text{ Hz}$, 8H, CH_2], 7.53 [dd, $^3J(\text{H,H}) = 7.5 \text{ Hz}$, $^4J(\text{H,H}) = 1.4 \text{ Hz}$, 1H, Ar-H], 7.59 [dt, $^3J(\text{H,H}) = 7.5 \text{ Hz}$, $^4J(\text{H,H}) = 1.2 \text{ Hz}$, 1H, Ar-H], 7.68 [dt, $^3J(\text{H,H}) = 7.5 \text{ Hz}$, $^4J(\text{H,H}) = 1.2 \text{ Hz}$, 1H, Ar-H], 8.08 [dd, $^3J(\text{H,H}) = 8.2 \text{ Hz}$, $^5J(\text{P,H}) = 1.1 \text{ Hz}$, 1H, Ar-H], 9.56 [d, $^2J(\text{P,H}) = 3.8 \text{ Hz}$, 1H, NH]. ^{13}C NMR (125.76 MHz, CDCl_3): $\delta = 44.91$ [d, $^2J(\text{P,C}) = 1.6 \text{ Hz}$], 67.09 [d, $^3J(\text{P,C}) = 4.9 \text{ Hz}$], 124.35 (s), 128.68 (s), 130.68 (s), 132.73 [d, $^3J(\text{P,C}) = 10.2 \text{ Hz}$], 133.53 (s), 146.39 (s), 167.70 (s). ^{31}P NMR (202.46 MHz, CDCl_3): $\delta = 10.49$ (m). IR (KBr, cm^{-1}): 3425, 3045 ($\nu\text{N-H}$), 2935, 1682 ($\nu\text{C=O}$), 1521, 1445, 1355, 1186 ($\nu\text{P=O}$), 1125, 967, 853 ($\nu\text{P-N}$), 824 ($\nu\text{P-N}$), 733 ($\nu\text{P-N}$). Anal.: calc. for $\text{C}_{15}\text{H}_{21}\text{N}_4\text{O}_6\text{P}$: C 46.9, H 5.5, N 14.6%; found: C 47.1, H 5.7, N 14.5%.

2.3.10. *N*-(3-Nitrobenzoyl)-*N'*,*N''*-bis(morpholino)phosphoric triamide (8). Yield: 76%, m.p. 482 K. ^1H NMR (500.13 MHz, CDCl_3): $\delta = 3.28$ (m, 4H, CH_2), 3.34 (m, 4H, CH_2), 3.66 [t, $^3J(\text{H,H}) = 4.6 \text{ Hz}$, 8H, CH_2], 7.67 [t, $^3J(\text{H,H}) = 8.0 \text{ Hz}$, 1H, Ar-H], 8.41 [ddd, $^3J(\text{H,H}) = 8.2 \text{ Hz}$, $^4J(\text{H,H}) = 0.9 \text{ Hz}$, $^7J(\text{P,H}) = 1.1 \text{ Hz}$, 1H, Ar-H], 8.48 [dt, $^3J(\text{H,H}) = 7.8 \text{ Hz}$, $^5J(\text{P,H}) = 1.4 \text{ Hz}$, 1H, Ar-H], 9.43 [t, $^5J(\text{P,H}) = 1.9 \text{ Hz}$, 1H, Ar-H], 10.43 [d, $^2J(\text{P,H}) = 4.5 \text{ Hz}$, 1H, NH]. ^{13}C NMR (125.76 MHz, CDCl_3): $\delta = 45.17$ [d, $^2J(\text{P,C}) = 1.6 \text{ Hz}$], 67.14 [d, $^3J(\text{P,C}) = 5.0 \text{ Hz}$], 123.68 (s), 127.02 (s), 129.52 (s), 134.69 [d, $^3J(\text{P,C}) = 9.2 \text{ Hz}$], 134.91 (s), 148.49 (s), 166.10 [d, $^2J(\text{P,C}) = 2.6 \text{ Hz}$]. ^{31}P NMR (202.46 MHz, CDCl_3): $\delta = 11.64$ (m). IR (KBr, cm^{-1}): 3425, 3065 ($\nu\text{N-H}$), 2940, 1670 ($\nu\text{C=O}$), 1520, 1434, 1345, 1178 ($\nu\text{P=O}$), 1130, 967, 862 ($\nu\text{P-N}$), 821 ($\nu\text{P-N}$), 720 ($\nu\text{P-N}$). Anal.: calc. for $\text{C}_{15}\text{H}_{21}\text{N}_4\text{O}_6\text{P}$: C 46.9, H 5.5, N 14.6%; found: C 46.7, H 5.4, N 14.8%.

2.3.11. *N*-(4-Nitrobenzoyl)-*N'*,*N''*-bis(morpholino)phosphoric triamide (9). Yield: 87%, m.p. 510 K. ^1H NMR (500.13 MHz, CDCl_3): $\delta = 3.24$ (m, 4H, CH_2), 3.30 (m, 4H, CH_2), 3.32 [t, $^3J(\text{H,H}) = 4.6 \text{ Hz}$, 8H, CH_2], 8.28 [d, $^3J(\text{H,H}) = 8.8 \text{ Hz}$, 2H, Ar-H], 8.32 [d, $^3J(\text{H,H}) = 8.8 \text{ Hz}$, 2H, Ar-H], 9.72 [d, $^2J(\text{P,H}) = 4.3 \text{ Hz}$, 1H, NH]. ^{13}C NMR (125.76 MHz, CDCl_3): $\delta = 45.14$ [d, $^2J(\text{P,C}) = 1.5 \text{ Hz}$], 67.10 [d, $^3J(\text{P,C}) = 5.0 \text{ Hz}$], 123.58 (s), 129.68 (s), 138.32 [d, $^3J(\text{P,C}) = 9.1 \text{ Hz}$], 150.29 (s), 166.36 (s). ^{31}P NMR (202.46 MHz, CDCl_3): $\delta = 11.73$ (m). IR (KBr, cm^{-1}): 3430, 3090 ($\nu\text{N-H}$), 2835, 1672 ($\nu\text{C=O}$), 1516, 1441, 1347, 1196 ($\nu\text{P=O}$), 1100, 964, 845 ($\nu\text{P-N}$), 818 ($\nu\text{P-N}$), 722 ($\nu\text{P-N}$) cm^{-1} . Anal.: calc. for $\text{C}_{15}\text{H}_{21}\text{N}_4\text{O}_6\text{P}$: C 46.9, H 5.5, N 14.6%; found: C 46.6, H 5.3, N 14.8%.

2.3.12. $\text{La}(\text{NO}_3)_3(\text{H}_2\text{O})(\text{CO}(\text{CH}_3)_2)[(p\text{-NO}_2)\text{C}_6\text{H}_4\text{CONHPO}(\text{NC}_4\text{H}_8\text{O})_2]_2$ (10). Yield: 80%, m.p. 445 K. ^1H NMR (500.13 MHz, d_6 -DMSO): $\delta = 3.36$ (br, 16H, CH_2), 3.54 (br, 16H, CH_2), 8.10 [d, $^3J(\text{H,H}) = 7.0 \text{ Hz}$, 4H, Ar-H], 8.29 [d, $^3J(\text{H,H}) = 6.9 \text{ Hz}$, 4H, Ar-H], 9.66 (s, 2H, NH). ^{13}C NMR (125.76 MHz, d_6 -DMSO): $\delta = 44.36$ (s), 66.34 [d, $^3J(\text{P,C}) =$

Table 1

Selected NMR data of (1)–(9).

$R^1 = 2\text{-NO}_2\text{-C}_6\text{H}_4\text{C(O)NH}$, $R^2 = 3\text{-NO}_2\text{-C}_6\text{H}_4\text{C(O)NH}$, $R^3 = 4\text{-NO}_2\text{-C}_6\text{H}_4\text{C(O)NH}$, $X^1 = \text{N}(\text{C}_2\text{H}_5)_2$, $X^2 = \text{NC}_4\text{H}_8$, $X^3 = \text{NC}_4\text{H}_8\text{O}$.

Series	No.	Compound	$\delta(^{31}\text{P})$ (p.p.m.)	$\delta(^{13}\text{C})_{\text{carbonyl}}$ (p.p.m.)	$^2J(\text{P,C})_{\text{aliphatic}}$ (Hz)	$^3J(\text{P,C})_{\text{aliphatic}}$ (Hz)	$^3J(\text{P,C})_{\text{aromatic}}$ (Hz)	CH ₂ pattern†
S1	(1)	$R^1\text{P(O)}(\text{X}^1)_2$	14.26	167.39	5.2	2.7	9.3	m
	(2)	$R^2\text{P(O)}(\text{X}^1)_2$	15.43	166.27	5.2	2.7	9.5	m
	(3)	$R^3\text{P(O)}(\text{X}^1)_2$	15.47	166.50	5.2	2.4	9.2	m
S2	(4)	$R^1\text{P(O)}(\text{X}^2)_2$	8.69	167.43	5.2	8.3	8.9	2m
	(5)	$R^2\text{P(O)}(\text{X}^2)_2$	9.79	166.15	5.4	8.3	9.2	2m
	(6)	$R^3\text{P(O)}(\text{X}^2)_2$	9.88	166.45	5.3	8.3	8.8	2m
S3	(7)	$R^1\text{P(O)}(\text{X}^3)_2$	10.49	167.70	1.6	4.9	10.2	m
	(8)	$R^2\text{P(O)}(\text{X}^3)_2$	11.64	166.10	1.6	5.0	9.2	2m
	(9)	$R^3\text{P(O)}(\text{X}^3)_2$	11.73	166.36	1.5	5.0	9.1	2m

† The CH₂ protons revealed one multiplet (m) or two multiplet (2m) signals in ¹H NMR spectra.

5.4 Hz], 123.31 (s), 129.65 (s), 149.44 (s), 167.14 (s). ³¹P NMR (202.46 MHz, *d*₆-DMSO): $\delta = 8.73$ (m). IR (KBr, cm⁻¹): 3325 ($\nu\text{N-H}$), 2945, 1692 ($\nu\text{C=O}$), 1518, 1443, 1345, 1155 ($\nu\text{P=O}$), 1104, 969, 841 ($\nu\text{P-N}$), 811 ($\nu\text{P-N}$), 729 ($\nu\text{P-N}$). Anal.: calc. for C₃₃H₅₀LaN₁₁O₂₃P₂: C 33.9, H 4.3, N 13.2; found: C 34.1, H 4.6, N 13.0%.

2.3.13. **Sm(NO₃)₃(H₂O)[(p-NO₂)C₆H₄CONHPO(NC₄H₈O)₂]₂ (11).** Yield: 78%, d.p. 433 K. ¹H NMR (500.13 MHz, CD₃CN): $\delta = 2.08$ (s, 2H, OH₂), 3.55 (s, 16H, CH₂), 3.73 (s, 16H, CH₂), 7.95 [d, ³J(H,H) = 7.0 Hz, 4H, Ar-H], 8.20 [d, ³J(H,H) = 7.0 Hz, 4H, Ar-H], 9.28 (s, 2H, NH). ¹³C NMR (125.76 MHz, CD₃CN): $\delta = 46.11$ (s), 67.56 (s), 124.75

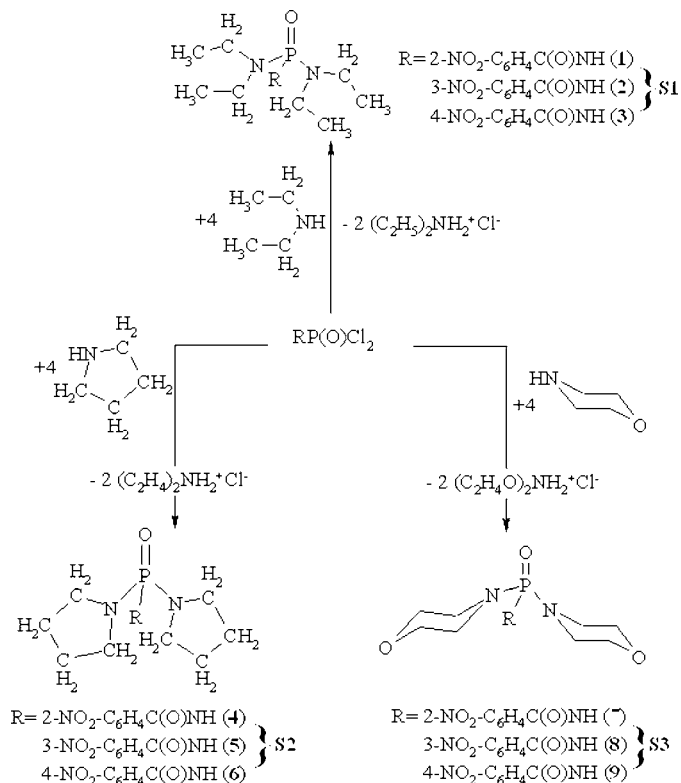


Figure 1
Preparation pathway for (1)–(9).

(s), 130.61 (s), 151.77 (s). ³¹P NMR (202.46 MHz, CD₃CN): $\delta = 7.04$ (br). IR (KBr, cm⁻¹): 3345 ($\nu\text{N-H}$), 2865, 1698 ($\nu\text{C=O}$), 1525, 1490, 1468, 1345, 1253, 1162 ($\nu\text{P=O}$), 1107, 974, 842 ($\nu\text{P-N}$), 734 ($\nu\text{P-N}$), 709 ($\nu\text{P-N}$) cm⁻¹.

2.3.14. **Eu(NO₃)₃(H₂O)[(p-NO₂)C₆H₄CONHPO(NC₄H₈O)₂]₂ (12).** Yield: 75%, d.p. 437 K. ¹H NMR (500.13 MHz, CD₃CN): $\delta = 1.02$ (s, 16H, CH₂), 2.06 (s, 2H, OH₂), 2.80 (s, 16H, CH₂), 5.60 (br, 2H, NH), 8.65 (s, 4H, Ar-H), 8.83 (s, 4H, Ar-H). ¹³C NMR (125.76 MHz, CD₃CN): $\delta = 43.43$ (s), 65.47 (s), 124.22 (s), 130.33 (s), 152.04 (s). ³¹P

NMR (202.46 MHz, CD₃CN) $\delta = -128.10$ (br). IR (KBr, cm⁻¹): 3345 ($\nu\text{N-H}$), 2865, 1699 ($\nu\text{C=O}$), 1525, 1491, 1447, 1344, 1296, 1249, 1162 ($\nu\text{P=O}$), 1139, 1105, 973, 917, 853 ($\nu\text{P-N}$), 735 ($\nu\text{P-N}$), 708 ($\nu\text{P-N}$), 518, 493 cm⁻¹.

2.3.15. **Er(NO₃)₃(H₂O)[(p-NO₂)C₆H₄CONHPO(NC₄H₈O)₂]₂ (13).** Yield: 83%, m.p. 458 K. ¹H NMR (500.13 MHz, *d*₆-DMSO): $\delta = 0.50$ –7.40 (br), 8.50–13.50 (br). ³¹P NMR (202.46 MHz, *d*₆-DMSO): $\delta = 8.41$ (br). IR (KBr, cm⁻¹): 3330 ($\nu\text{N-H}$), 2950, 1687 ($\nu\text{C=O}$), 1515, 1442, 1347, 1301, 1256, 1155 ($\nu\text{P=O}$), 1099, 970, 842 ($\nu\text{P-N}$), 733 ($\nu\text{P-N}$), 704 ($\nu\text{P-N}$), 492 cm⁻¹. Anal.: calc. for C₃₀H₄₄ErN₁₁O₂₂P₂: C 31.6, H 3.9, N 13.5; found: C 31.4, H 4.1, N 13.3%.

3. Results and discussion

3.1. Spectroscopic study

The new phosphoric triamides (1)–(9) (Fig. 1) and four lanthanide(III) complexes of *N*-(4-nitrobenzoyl)-*N,N'*-bis(morpholino) phosphoric triamide (10)–(13) (Fig. 2) were prepared. All the compounds contain two identical secondary amine groups connected to the P atom. Compounds (1)–(9) can be split into three series, S1, S2 and S3, according to the type of secondary amine group, see Fig. 1. Selected spectroscopic data of these compounds are listed in Table 1.

Compounds S1, S2 and S3 contain a –P–N–CH₂– skeleton, in which these protons are diastrotopic. In the S1-type molecules, containing acyclic aliphatic amines, the rotation around the P–N bond is fast and the CH₂ protons revealed one multiplet signal in ¹H NMR spectra. On the

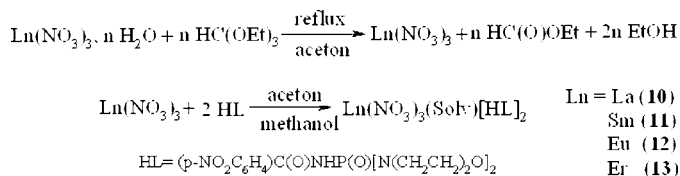


Figure 2
Preparation pathway for (10)–(13).

Table 2

Crystallographic data for (3) and (5).

Experiments were carried out with Mo $K\alpha$ radiation.

	(3)	(5)
Crystal data		
Chemical formula	C ₁₅ H ₂₅ N ₄ O ₄ P	C ₁₅ H ₂₁ N ₄ O ₄ P
M_r	356.36	352.3
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Temperature (K)	120	120
a, b, c (Å)	9.9548 (8), 20.3681 (16), 8.8471 (7)	9.1631 (2), 9.3224 (2), 11.4353 (3)
α, β, γ (°)	90, 96.125 (2), 90	109.909 (2), 110.445 (2), 96.024 (2)
V (Å ³)	1783.6 (2)	832.33 (4)
Z	4	2
μ (mm ⁻¹)	0.18	0.19
Crystal size (mm)	0.30 × 0.26 × 0.22	0.98 × 0.36 × 0.22
Data collection		
Diffractometer	Bruker SMART 1000 CCD area detector	Oxford Diffraction CCD
Absorption correction	Multi-scan <i>SADABS</i>	Multi-scan <i>CrysAlis</i>
T_{\min}, T_{\max}	0.945, 0.963	0.942, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16 991, 3882, 2498	10 200, 3460, 2983
R_{int}	0.055	0.016
Completeness (%)	99.6	98.1
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.056, 0.123, 1.09	0.035, 0.096, 3.18
No. of reflections	3882	3460
No. of parameters	221	225
No. of restraints	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.37, -0.29	0.49, -0.44

Computer programs used: *SMART* (Bruker, 1998b), *CrysAlis CCD* (Oxford Diffraction, 2007b), *X-AREA, X-RED* (Stoe & Cie, 2006), *SAINTE-Plus* (Bruker, 1998a), *CrysAlis RED* (Oxford Diffraction, 2007a), *SHELXTL, SHELXS97, SHELXS97* (Sheldrick, 2008), *SUPERFLIP* (Palatinus & Chapuis, 2007), *JANA2006* (Petrick *et al.*, 2006), *DIAMOND* (Brandenburg & Putz, 2005), *ORTEP3* (Farrugia, 1997), *PLATON* (Spek, 2009).

other hand, the slow P–N rotation and inflexible ring inversion in compounds of S2 type containing five-membered ring amines, is confirmed by the existence of two separated multiple signals for the endocyclic CH₂ protons. These protons are diastereotopic, coupled with each other, their corresponding P atoms and their neighboring protons. In compounds containing flexible cyclic amine groups (S3) the two separated signals are coalesced [in (7)] or adjacent [in (8) and (9)] to each other. Therefore, the P–N_{amine} rotation and ring inversion affect the coupling patterns of diastereotopic methylene protons in ¹H NMR spectra (Gholivand, Mostaanzadeh *et al.*, 2006).

Owing to the presence of paramagnetic cations (Eu³⁺ and Er³⁺) the ¹H NMR spectra of complexes (12) and (13) show broadened signals for all the aliphatic and aromatic protons. Surprisingly, in (13) the width of two observed signals is approximately 6 p.p.m.

The ¹³C NMR of compounds S2 and S3, which contain cyclic amine groups, show that ³*J*(P,C_{amine}) > ²*J*(P,C_{amine}), but in compounds containing an acyclic amine (S1) ²*J*(P,C_{amine}) > ³*J*(P,C_{amine}). The rotation around the C–N_{amine} bond in molecules of type S1 changes the ∠ PNCC dihedral angles (the average of ∠ PNCC dihedral angle values are near to 90°) and it causes the decrease in ³*J*(P,C_{amine}) values of these

compounds. Compounds of the type S2 and S3 do not show any C–N_{amine} bond rotation, therefore the ∠ PNCC dihedral angle values are approximately 180°, and considering the Karplus relationship (Karplus, 1963) it confirms the high values of ³*J*(P,C_{amine}). As shown in Table 1, with increasing the ring size of the amine groups in S2 and S3 compounds, the ³*J*(P,C_{amine}) becomes smaller reaching about 8.3 and 4.9 Hz in compounds containing five- and six-membered ring amine groups, respectively. This is in agreement with the reported results in the similar phosphoric triamides (Gholivand, Shariatnia & Pourayoubi, 2006). The lowest ²*J*(P,C_{amine}) is related to compounds S3, probably due to the distance between the P and C atoms and the ∠ PNC bond angle. The lowest ³*J*(P,C_{amide}) in each series of the analogous compounds S1, S2 and S3 is observed for the 4-NO₂–C₆H₄C(O)N(H)P(O)(X)₂ formula.

³¹P NMR indicates that δ(³¹P) in compounds S1 (containing acyclic amine groups) is higher than in those of compounds S2 and S3 (containing cyclic amine groups), and also with increasing the ring size of amine groups it shifts to down field. In each

series of analogous compounds RC(O)N(H)P(O)(X)₂: (S1–S3), the δ(³¹P) and δ(¹³C=O) values are decreased as R = 4-NO₂–C₆H₄ > 3-NO₂–C₆H₄ > 2-NO₂–C₆H₄ and 2-NO₂–C₆H₄ > 4-NO₂–C₆H₄ > 3-NO₂–C₆H₄, respectively.

Owing to the presence of paramagnetic cations (Sm³⁺, Eu³⁺ and Er³⁺) the ³¹P NMR spectra of complexes (11)–(13) show broadened signals. In (12) this signal shifts to unexpected high fields [δ(³¹P) = -128.10 p.p.m.].

The IR spectra of compounds S1 and S2 show the presence of characteristic vibrational modes for chemical groups in the molecule (Gholivand *et al.*, 2007). The high frequency range with strong absorptions at typically *ca* 3030 cm⁻¹ can be assigned with confidence to the ν(N–H) stretching of the –C(O)NH– moiety. It is interesting to note that in each series of S1–S3 compounds, the ν(N–H) frequencies of the 4-nitrobenzoyl substitute molecules have the highest values, reaching 3090 cm⁻¹ in (9). Strong intensity bands appear in the spectra at frequency values of *ca* 1590 and 1350 cm⁻¹, characteristic for the antisymmetric and symmetric stretching modes of the nitro group, respectively. The C=O frequencies in all phosphoramidates (1)–(9) are in the range 1669 [(3), (5)] to 1682 cm⁻¹. The P=O frequency values in S1 and S2 compounds are very close to each other, with typical values around 1210 cm⁻¹. Other characteristic fundamentals for

Table 3

Crystallographic data for (9), (10) and (13).

Experiments were carried out with Mo $K\alpha$ radiation.

	(9)	(10)	(13)
Crystal data			
Chemical formula	C ₁₅ H ₂₁ N ₄ O ₆ P	C ₃₃ H ₅₀ LaN ₁₁ O ₂₃ P ₂	C ₃₀ H ₄₄ ErN ₁₁ O ₂₂ P ₂ ·0.5·0.5C ₃ H ₆ O·0.5CH ₄ O
M_r	384.33	1169.7	1185.02
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	120	100	173
a, b, c (Å)	16.2973 (12), 11.1318 (8), 9.4354 (7)	8.8631 (10), 33.466 (4), 15.5399 (18)	8.7152 (4), 33.5889 (14), 15.3815 (8)
β (°)	94.881 (2)	93.195 (3)	92.113 (4)
a, b, c (Å)	16.2973 (12), 11.1318 (8), 9.4354 (7)	8.8631 (10), 33.466 (4), 15.5399 (18)	8.7152 (4), 33.5889 (14), 15.3815 (8)
β (°)	94.881 (2)	93.195 (3)	92.113 (4)
V (Å ³)	1705.5 (2)	4602.2 (9)	4499.6 (4)
Z	4	4	4
μ (mm ⁻¹)	0.20	1.10	2.03
Crystal size (mm)	0.28 × 0.26 × 0.18	0.47 × 0.33 × 0.20	0.33 × 0.27 × 0.21
Data collection			
Diffractometer	Bruker SMART 1000 CCD area detector	Bruker SMART 1000 CCD area detector	STOE IPDS2
Absorption correction	Multi-scan <i>SADABS</i>	Multi-scan <i>SADABS</i>	Multi-scan <i>MULScanABS</i>
T_{\min} , T_{\max}	0.941, 0.968	0.657, 0.801	0.607, 0.657
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19 538, 4958, 3709	54 317, 12 056, 9147	42 064, 8492, 6850
R_{int}	0.032	0.087	0.045
Completeness (%)	99.6	98.7	99.2
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.126, 1.05	0.055, 0.112, 1.01	0.042, 0.109, 1.03
No. of reflections	4958	12 056	8492
No. of parameters	247	687	590
No. of restraints	11	0	5
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	Mixture of independent and constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.45, -0.41	1.32, -1.44	2.07, -1.59

carbacylamidophosphate species are the N–P stretching modes, typically observed at frequency values slightly lower than 850 cm⁻¹. These values are in good agreement with the reported vibrational data for related compounds (Iriarte *et al.*, 2008).

The IR spectra of the coordination compounds (10)–(13) reveal a significantly lower frequency of $\nu(\text{P}=\text{O})$ compared with the data for the free ligand (9) [$\Delta\nu(\text{P}=\text{O}) = 34\text{--}41\text{ cm}^{-1}$], reflecting the coordination through the phosphoryl O atom

(Gubina, Shatrava *et al.*, 2000; Trush *et al.*, 1999). For the $\nu(\text{C}=\text{O})$ value an opposite result was obtained [1687–1699 cm⁻¹ in complexes and 1672 cm⁻¹ in (9)]. The absorption band in the IR spectrum of the free ligand (9) at 3090 cm⁻¹ can be assigned to the vibrations of the NH group connected to a phosphoryl group of a neighboring molecule by a strong hydrogen bond (Gubina, Shatrava *et al.*, 2000; Amirkhanov, Ovchynnikov *et al.*, 1997). By coordination to the lanthanide

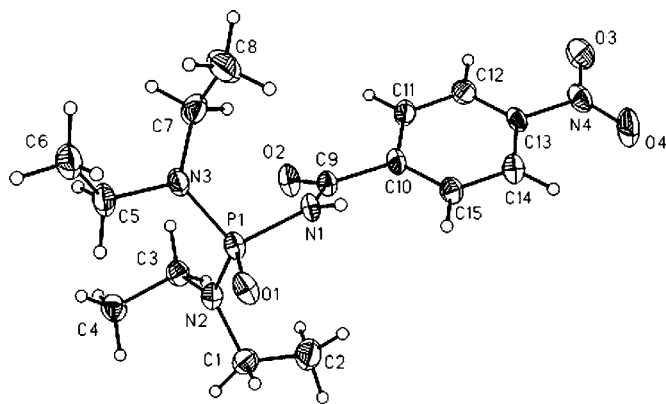


Figure 3
Molecular structure of (3), 4-NO₂–C₆H₄C(O)NHP(O)(N(C₂H₅)₂)₂, showing 50% probability displacement ellipsoids.

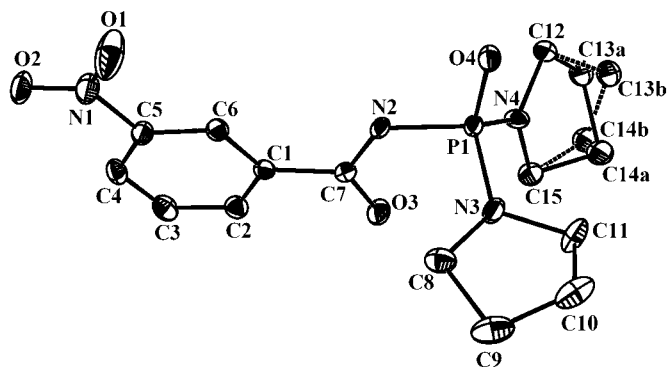


Figure 4
Molecular structure of (5), 3-NO₂–C₆H₄C(O)NHP(O)(NC₄H₈)₂, showing 50% probability displacement ellipsoids. H atoms are omitted for the sake of clarity.

Table 4
Selected bond lengths (Å) and angles (°) for (3), (5) and (9).

(3)		(5)		(9)	
P1–O1	1.486 (6)	P1–O4	1.4840 (14)	P1–O1	1.4811 (12)
P1–N2	1.637 (2)	P1–N4	1.6268 (16)	P1–N2	1.6251 (15)
P1–N1	1.693 (2)	P1–N3	1.6351 (10)	P1–N1	1.6443 (15)
P1–N3	1.632 (2)	P1–N2	1.6954 (14)	P1–N3	1.6875 (14)
O2–C9	1.221 (3)	O3–C7	1.223 (2)	O4–C9	1.220 (2)
N1–C9	1.370 (3)	N4–C15	1.478 (3)	N1–C1	1.470 (2)
N2–C1	1.475 (3)	N4–C12	1.4747 (18)	N1–C4	1.471 (2)
N2–C3	1.479 (3)	N3–C8	1.480 (2)	N2–C5A	1.4573 (18)
N3–C7	1.461 (3)	N3–C11	1.485 (2)	N2–C8B	1.472 (3)
N3–C5	1.469 (3)	N2–C7	1.373 (2)	N3–C9	1.377 (2)
O1–P1–N2	109.75 (10)	O4–P1–N4	110.38 (7)	O1–P1–N2	115.72 (8)
O1–P1–N1	105.43 (10)	O4–P1–N3	118.96 (7)	O1–P1–N1	109.59 (7)
N2–P1–N1	112.16 (10)	O4–P1–N2	105.02 (7)	N2–P1–N1	105.78 (8)
O1–P1–N3	116.39 (11)	N4–P1–N3	104.98 (7)	O1–P1–N3	112.74 (7)
N2–P1–N3	107.62 (11)	N4–P1–N2	114.44 (7)	N2–P1–N3	105.41 (7)
N1–P1–N3	105.49 (10)	N3–P1–N2	103.24 (6)	N1–P1–N3	107.03 (7)
C9–N1–P1	125.78 (17)	P1–N4–C15	128.41 (10)	C1–N1–P1	119.16 (11)
C1–N2–P1	118.66 (16)	P1–N4–C12	122.38 (13)	C4–N1–P1	123.18 (12)
C3–N2–P1	124.17 (17)	C15–N4–C12	109.19 (14)	C5A–N2–P1	128.95 (11)
C7–N3–P1	125.28 (17)	P1–N3–C8	124.07 (11)	C8B–N2–P1	122.4 (3)
C5–N3–P1	117.79 (18)	P1–N3–C11	121.00 (11)	C8A–N2–P1	115.6 (2)
C5–N3–C7	116.9 (2)	P1–N2–C7	124.81 (12)	C9–N3–P1	121.00 (11)
O1–P1–C9–O2	163.5 (8)	O4–P1–C7–O3	167.6 (1)	O1–P1–C9–O4	–51.0 (5)
P1–N2–C1–C2	–83.9 (2)	P1–N3–C8–C9	167.8 (5)	P1–N1–C1–C2	151.8 (9)
P1–N2–C3–C4	–121.2 (2)	P1–N3–C11–C10	144.1 (0)	P1–N1–C4–C3	–152.3 (4)
P1–N3–C5–C6	119.7 (2)	P1–N4–C12–C13a	175.1 (2)	P1–N3–C9–O4	–3.0 (8)
P1–N3–C7–C8	–81.2 (3)	P1–N4–C15–C14a	–146.91	P1–N3–C9–C10	176.9 (3)

ions, the $\text{P}=\text{O}\cdots\text{H}-\text{N}$ intermolecular hydrogen bonds are broken and the frequencies $\nu(\text{N}-\text{H})$ of complexes are detected at higher frequencies, in the $3325\text{--}3345\text{ cm}^{-1}$ range.

According to the TGA and DTA data the lanthanum complex (10) is stable up to 373 K. The endothermic two-stage elimination of acetone and water molecules is observed at 385 and 413 K, respectively. Two exothermic stages (at 449 and 552 K) correspond to the decomposition of the complex. It is

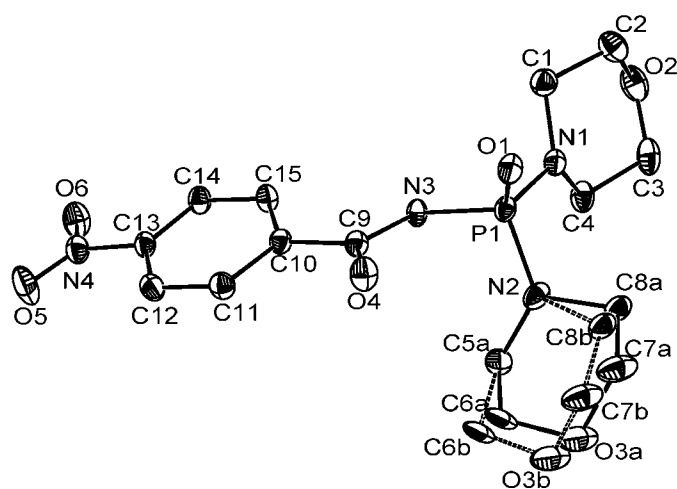


Figure 5
Molecular structure of (9), $4\text{-NO}_2\text{-C}_6\text{H}_4\text{C}(\text{O})\text{NHP}(\text{O})(\text{NC}_4\text{H}_8\text{O})_2$, showing 50% probability displacement ellipsoids.

bonded to P *via* N atoms. These compounds contain one amidic H atom and form centrosymmetric dimers [in (3) and (5)] and polymeric chains [in (9)] *via* intermolecular $\text{P}=\text{O}\cdots\text{H}-\text{N}$ hydrogen bonds (Table 6, Figs. 8 and 9). In

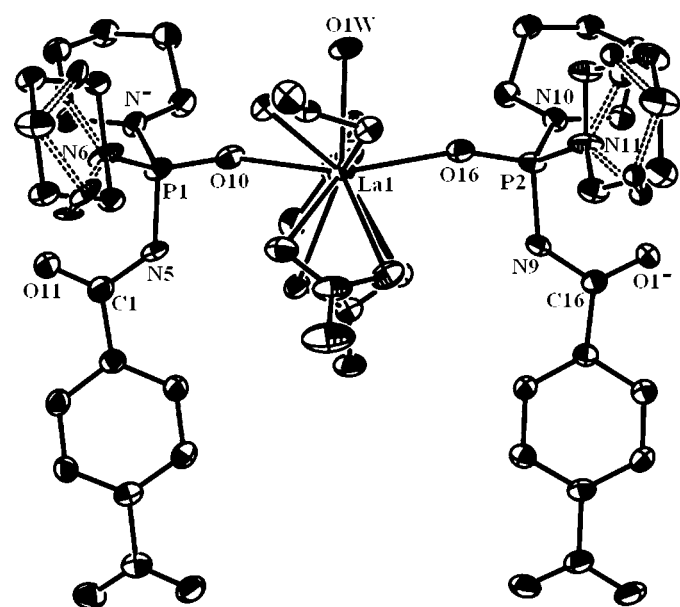


Figure 6
Molecular structure of (10), $\text{La}(\text{NO}_3)_3(\text{H}_2\text{O})[(\text{CH}_3)_2\text{CO}][4\text{-NO}_2\text{-C}_6\text{H}_4\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})(\text{NC}_4\text{H}_8\text{O})_2]_2$, showing 50% probability displacement ellipsoids.

interesting to note that the onset at 449 K of the major weight loss is very near the melting point of (10). The TGA of (13) reveals a weight loss up to 373 K owing to the presence of lattice solvent (acetone and methanol) in the solid. The endothermic stage elimination of water molecules is observed at 418 K. Two exothermic stages (at 447 and 554 K) correspond to the decomposition of the complex. The thermal analysis of (11) and (12) is similar to (13).

3.2. X-ray crystallography

Single crystals of (3), (5) and (9) were obtained from a solution of chloroform and acetonitrile (with ratio 4/1) at room temperature. The crystallographic data and the details of the X-ray analysis of (3), (5), (9), (10) and (13) are given in Tables 2 and 3, selected bond lengths and angles in Tables 4 and 5. Molecular structures of these compounds are shown in Figs. 3–7. Compounds (3), (5) and (9) consist of isolated molecules, each of them being composed of two amine groups and a nitrobenzoyl group

Table 5

Selected bond lengths (Å) and angles (°) for (10) and (13).

(10)		(13)	
La1—O10	2.402 (3)	Er1—O1	2.275 (3)
La1—O16	2.432 (3)	Er1—O7	2.249 (3)
La1—O1W	2.489 (3)	Er1—O1W	2.313 (4)
La1—O4	2.786 (3)	Er1—O13	2.445 (4)
La1—O7	2.608 (3)	Er1—O14	2.430 (4)
La1—O2	2.611 (3)	Er1—O16	2.487 (3)
La1—O8	2.623 (3)	Er1—O17	2.444 (4)
La1—O1	2.640 (3)	Er1—O19	2.383 (4)
La1—O5	2.642 (3)	Er1—O20	2.456 (6)
La1—O1S	2.605 (3)	P2—N5	1.684 (5)
P1—O10	1.493 (3)	P1—O1	1.493 (3)
P2—O16	1.489 (3)	P2—O7	1.491 (3)
P1—N7	1.618 (3)	P1—N1	1.677 (4)
O10—La1—O16	148.98 (10)	O1—Er1—O7	151.50 (13)
O10—La1—O1W	82.42 (10)	O1—Er1—O1W	80.46 (12)
O16—La1—O1W	77.39 (10)	O7—Er1—O1W	92.58 (12)
O10—La1—O1S	73.39 (10)	O1—Er1—O13	126.89 (11)
O16—La1—O1S	78.90 (10)	O1—Er1—O14	80.24 (11)
O1W—La1—O1S	75.62 (10)	O1—Er1—O16	74.38 (11)
O10—La1—O7	126.71 (10)	O1—Er1—O17	125.38 (12)
O16—La1—O7	81.77 (10)	O1—Er1—O19	83.98 (11)
O1W—La1—O7	144.20 (11)	O7—Er1—O13	75.51 (12)
O1S—La1—O7	128.23 (10)	O7—Er1—O14	126.64 (12)
O10—La1—O2	116.93 (10)	O7—Er1—O16	119.82 (12)
O16—La1—O2	81.24 (9)	O7—Er1—O17	75.36 (12)
O1W—La1—O2	77.11 (10)	O7—Er1—O19	79.77 (12)

contrast to all the similar phosphoro-azo compounds reported previously, the P=O···H and N—H···O hydrogen bonds have an *anti* orientation in (9) and the molecules are connected to each other *via* one hydrogen bond, see Fig. 9. It is worth mentioning that the *N*-benzoyl phosphoric triamides studied previously were found either in the form of dimeric aggregates (Gholivand *et al.*, 2005) or as polymeric chains (Gholivand, Mostaanazadeh *et al.*, 2006).

Phosphoro-azo derivatives of β -diketones can create different types of complexes (bidentate and monodentate) with a lanthanide ion. The complexation of (9) with lanthanum and erbium nitrate produced both a ten- and a ninefold coordination complex, (10) and (13), respectively, with two equal monodentate phosphoramidate ligands. This behavior contrasts with the coordination showed in neodymium complexes with the trichloroacetylphosphortriamide ligands, where the deprotonated form of the ligand acts in a bidentate

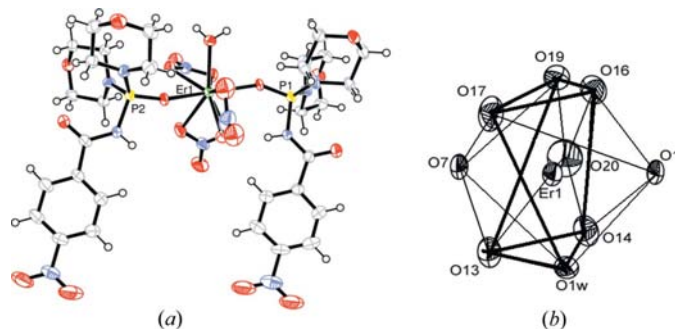


Figure 7

(a) Molecular structure of (13), $\text{Er}(\text{NO}_3)_3(\text{H}_2\text{O})[4\text{-NO}_2\text{-C}_6\text{H}_4\text{-C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})(\text{NC}_4\text{H}_8\text{O})_2]_2$, showing 50% probability displacement ellipsoids; (b) polyhedra of (13).

Table 6

Hydrogen bonds $D\text{—H}\cdots A$ for (3), (5), (9), (10) and (13) (Å, °).

	$D\text{—H}\cdots A$	$d(D\text{—H})$	$d(\text{H}\cdots A)$	$d(D\cdots A)$	$\angle \text{DHA}$
(3)	N1—H1N···O1 ⁱ	0.870	1.920	2.789 (3)	177.0
(5)	N2—H1N2···O4 ⁱⁱ	0.87	2.00	2.856	165.7
(9)	N3—H3N···O1 ⁱⁱⁱ	0.87	1.96	2.820 (5)	172.0
(10)	O1W—H1W1···O19 ^{iv}	0.890	1.943	2.810 (7)	164
	O1W—H2W1···O13 ^v	0.890	2.024	2.815 (6)	147
	N5—H5N···O5 ^{vi}	0.850	2.195	2.988 (5)	155
	N9—H9N···O4 ^{vi}	0.850	2.163	2.948 (5)	153
(13)	O1W—H1W···O5 ^{vii}	0.84 (5)	1.93 (5)	2.753 (5)	169 (7)
	O1W—H1W···O11 ^{viii}	0.84 (5)	2.01 (5)	2.807 (5)	158 (6)
	N1—H1N···O16 ^{vi}	0.86 (3)	2.11 (3)	2.887 (6)	150 (3)
	N1—H1N···O19 ^{vi}	0.86 (3)	2.53 (3)	3.184 (6)	134 (3)

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x, 2-y, 2-z$; (iii) $x, -y-\frac{1}{2}, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y-\frac{1}{2}, z-\frac{1}{2}$; (v) $x-\frac{1}{2}, -y-\frac{1}{2}, z+\frac{1}{2}$; (vi) x, y, z ; (vii) $-1+x, y, z$; (viii) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$.

manner *via* the O atoms of the phosphoryl and the carbonyl groups (Znovjyak *et al.*, 2009). In (10) the coordination sphere of the La^{3+} ion is a decatetrahedron (Fig. 6) comprising two P=O groups, acetone, water and three bidentate nitrate groups. Fig. 7 shows that the coordination sphere of the Er^{3+} ion in (13) is a tricapped trigonal prism. In both complexes one of the nitrate groups also participates in an intramolecular hydrogen bond to the N—H moiety of the phosphoramidate ligands. The nitrate groups symmetrically coordinate the central atom, therefore, the coordination polyhedron of $\text{La}(\text{NO}_3)_3(\text{H}_2\text{O})[(\text{CH}_3)_2\text{CO}][(\text{9})]_2$ and $\text{Er}(\text{NO}_3)_3(\text{H}_2\text{O})[(\text{9})]_2$ can be described as a distorted pseudo-pentagonal bipyramidal and pseudo-octahedron, respectively, provided that

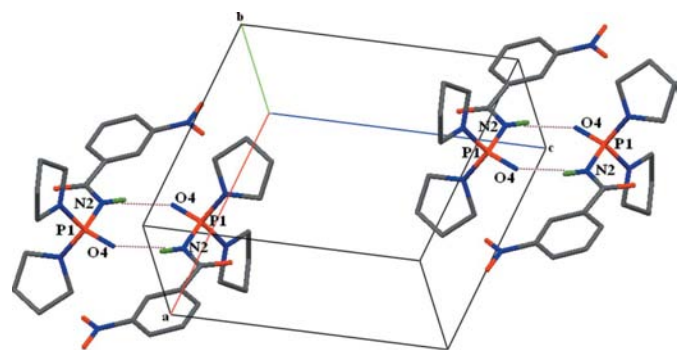


Figure 8

A view of the crystal structure of (5), in which the hydrogen bonds produced centrosymmetric dimmers.

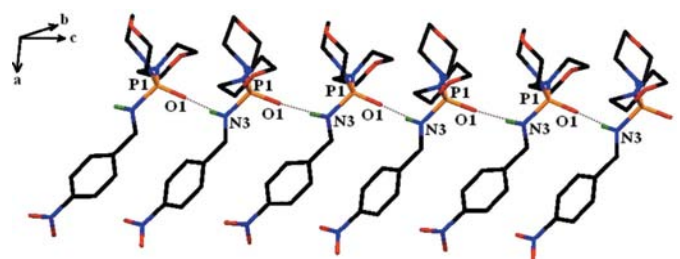


Figure 9

A view of part of the crystal structure of (9) in which the intermolecular hydrogen bond produced the one-dimensional polymeric chain.

each nitrate group occupies one site (the midpoint of the line connecting the coordinated O atoms of the nitrate group) in the coordination polyhedron. In the configuration of (10) the three nitrate groups, water and acetone occupy five equatorial positions with average bond angle of 72° , and the two phosphoramidate ligands are nearly in apical positions with bond angles of 149° . In the configuration of (13) the three nitrate groups and water occupy four equatorial positions with the average bond angle of 90° , and the two phosphoramidate ligands are nearly in apical positions with bond angles of 151.5° . In the planar four-membered rings of LnO_2N chelate, the average LaON angle is 97 and 95° , and the average $\text{Ln}-\text{O}$ bond length for the nitrate groups is 2.651 and 2.441 Å, in (10) and (13), respectively. In the crystal structures of both complexes intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds lead to the formation of two-dimensional polymeric chains (Table 6).

Amongst all known phosphoramidate compounds, the free ligand (9) is the first example in which the $-(\text{O})\text{C}-\text{NH}-\text{P}(\text{O})-$ skeleton has the *cisoid* conformation (the dihedral angle $\angle \text{OPCO}$ is -51.05°). It is interesting that in complexes of the same ligand the $(\text{O})\text{CNP}(\text{O})$ skeleton has the *anti* conformation [the average of two dihedral angles $\angle \text{OPCO}$ is -177.09° in (10) and -170.76° in (13)]. The individual intermolecular hydrogen bonds in the crystal of the free ligand (9) may be the cause of a unique dihedral angle $\angle \text{OPCO}$ ($\text{C}=\text{O}$ and $\text{P}=\text{O}$ double bonds in the *cisoid* position with respect to each other), see Fig. 8. On the other hand, in (3) and (5) the $\text{P}(\text{O})$ and $\text{C}(\text{O})$ groups are in an *anti* position with respect to each other, following the usual behavior found for other phosphoro-azo derivatives of β -diketones (Corbridge, 1995). The coordination environment of phosphorus is nearly tetrahedral, with the bond angles ranging from 103.1 (10) to 118.9 (5) $^\circ$, for angles $\text{O}10-\text{P}1-\text{N}5$ and $\text{O}4-\text{P}1-\text{N}3$, respectively. In these compounds, the $\text{P}-\text{N}_{\text{amide}}$ bond lengths [N_{amide} is the N atom of the $\text{P}(\text{O})\text{N}(\text{H})\text{C}(\text{O})$ moiety] are longer than the $\text{P}-\text{N}_{\text{amine}}$ bond lengths [N_{amine} is the N atom of the $\text{P}(\text{O})\text{NR}$ moiety], because of the electrostatic interaction of the N_{amide} lone pair with the $\text{C}=\text{O}$ π^* system that causes a partial multiple bond character in $\text{C}-\text{N}_{\text{amide}}$ (the $\text{C}-\text{N}_{\text{amide}}$ bond length is shorter than the $\text{C}-\text{N}_{\text{amine}}$ bond lengths). All of these bonds are shorter than the typical $\text{P}-\text{N}$ single bond (1.77 Å for $\text{NaHPO}_3\text{NH}_2$; Corbridge, 1995). The shortening may be related to an electrostatic effect (polar bond), which overlaps with the $\text{P}-\text{N}$ σ bond (Gilheany, 1994). The $\text{P}=\text{O}$ bond lengths in (3), (5), (9), (10) and (13) are 1.487 (6), 1.484 (1), 1.481 (1), [1.489 (3), 1.493 (3)] and [1.491 (3), 1.493 (3)] Å, respectively, and are slightly longer than the normal $\text{P}=\text{O}$ bond length (1.45 Å for POCl_3 ; Corbridge, 1995). The $\text{P}=\text{O}$ bond lengths in complexes (10) and (13) are larger than those in the corresponding ligand (9), but the $\text{C}=\text{O}$ and $\text{P}-\text{N}_{\text{amine}}$ bond lengths show an opposite result, Table 5. The sum of the angles around the N atoms in phosphoramidates are close to 360° (sp^2 -hybridization), which is caused by the delocalization of the lone pair of electrons of the nitrogen. This fact and the decrease in $\text{P}-\text{N}_{\text{amine}}$ distances in the coordinated ligand (10) and (13) compared with the free ligand (9) (*ca* 1.62 Å in the complexes, *versus ca* 1.63 Å in the

free ligand) can be explained by an increase in the electrostatic effect (polar bond), which overlaps with the $\text{P}-\text{N}_{\text{amine}}$ σ bonds upon complex formation.

The X-ray powder diffraction of the bulk samples of (9), (10) and (13) match with the simulated diffraction pattern from the single-crystal diffraction data, as shown in the supplementary material.¹

3.3. Quantum chemical calculations

Prompted by the unusual *cisoid* conformation found for (9) in the crystalline state, we decided to examine the molecular structure of the studied compounds by using quantum chemical calculations at the B3LYP/6-31+G* level of approximation. The main objective was to identify the possible effects of crystal packing on the preferred molecular conformation by comparing the experimental X-ray results with the corresponding computed structure for the molecule isolated in a vacuum (Gholivand *et al.*, 2008; Gholivand, Orouzadeh *et al.*, 2009). Different feasible conformations – formally produced by rotation around the $\text{P}-\text{N}$ dihedral angle of the $\text{O}=\text{C}-\text{N}(\text{H})-\text{P}=\text{O}$ group – have been analyzed for (3), (5) and (9) (for which experimental structural data are available). In all of these computed species the most stable form corresponds to a structure adopting an *anti* conformation around the $\text{N}-\text{P}$ single bond [the $\text{P}=\text{O}$ double bond in an *anti* orientation with respect to the $\text{N}-\text{C}(\text{O})$ single bond]. For better references, in such structures the $\text{C}=\text{O}$ and $\text{P}=\text{O}$ groups are in a nearly perfect antiperiplanar mutual orientation (Gholivand, Mostaanazadeh *et al.*, 2009). The $\text{O}=\text{P}-\text{N}-\text{C}$ dihedral angle values computed for (3) and (5) are 165.9 and 171.1° , in very good agreement with the experimentally determined: 161.1 (6) and 171.1 (2) $^\circ$, respectively. The *cisoid* conformation computed for (9) is characterized by a $\text{O}=\text{P}-\text{N}-\text{C}$ dihedral angle of 46.0° with the angle formed by the plane containing the $\text{P}=\text{O}$ and $\text{C}=\text{O}$ bonds being -60.3° , close to the experimental value of -51.0 (5) $^\circ$.

The computed energy differences between the most stable *anti* form and the *cisoid* conformation are 19.13 , 19.72 and 20.26 kJ mol^{-1} for (3), (5) and (9), respectively (electronic energy values corrected by vibrational zero-point energy). These values suggest that the substituent amine group attached to the phosphoryl group exert a minor effect on the idealized gas-phase conformational properties.

These results strongly suggest that the conformational inversion found in (9) for the central dihedral angle around the phosphoramidate moiety could be attributable to the presence of packing effects. In particular, the chain motif found in the crystal of (9), with the distinctive $\text{P}=\text{O}\cdots\text{H}-\text{N}$ intermolecular hydrogen-bond pattern shown in Fig. 9, could be responsible for the exceptional conformational preference found in the solid phase. Such a decisive influence in the

¹ Supplementary data for this paper, including selected ^1H , ^{13}C and ^{31}P NMR and IR spectra for the title compounds are given as supplementary information [XRD patterns simulated from single-crystal X-ray data and bulk materials for (9), (10) and (13) are also given], are available from the IUCr electronic archives (Reference: PS5006). Services for accessing these data are described at the back of the journal.

conformational properties exerted by the hydrogen bond has been largely reported in the literature for biomolecules (Coll *et al.*, 1987; Szewczak *et al.*, 1993) and also for related alkyl-phosphoryl compounds (Genov *et al.*, 1998).

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