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# Structures of a novel phosphoric triamide and its organotin(IV) complex

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ABSTRACT

A new phosphoric triamide 4-$NO_2C_6H_4NHP(O)(NC_4H_8O)_2$ (**1**) and its organotin(IV) complex $SnCl(C_6H_5)_3[4\text{-}NO_2C_6H_4NHP(O)(NC_4H_8O)_2]$ (**2**) were synthesized and characterized by $^{31}P$, $^{1}H$, $^{13}C$ NMR, IR spectroscopy and elemental analysis. The crystal structures of compounds **1** and **2** were determined by X-ray crystallography. Both compounds crystallize in monoclinic crystal system with $P2_1/n$ space group. The structure of **1** contains two symmetrically independent molecules while for **2** only one independent molecule is present with a five-coordinated tin(IV) in a distorted trigonal bipyramidal configuration. Strong intermolecular N–H···O and N–H···Cl hydrogen bonds together with weak intermolecular C–H···O hydrogen bonds connect molecules of **1** and **2** into 3D networks. Both compounds were also prepared as nanoparticles of the size 15–20 nm and a spherical morphology, as confirmed by SEM micrographs.



## 1. Introduction

Phosphoramide derivatives belong to a famous drugs family showing prominent anti-HIV [1], anti-HCV [2,3], antibacterial [4], antitumor and anticancer activities [5,6] as well as they act as enzyme inhibitors [7]. They are also efficient catalysts in chemical reactions [8,9]. The crystal structures of some phosphoramide molecules with two [10–12] and four [13,14] independent molecules in the crystal packing and an organotin(IV) complex [15] including two independent molecules were reported. The organotin(IV) complexes as are known for their important applications as antibacterial and anticancer [16–18], antifungal agents [19,20], as well as catalysts [21]. It should also be noted that most of the organotin(IV) complexes with phosphoramide ligands are six coordinated [14,15,22] and a few are five coordinated [23]. Recently, the preparation of nanosized compounds has become of great interest due to the prominent properties at this scale including large specific surface areas and enhanced optical [24], electrical [25,26] and medical performance [27,28]. The nanoparticles of some organotin(IV) complexes of phosphoramides have been synthesized using ultrasonic method [29].

In this work, a new phosphoric triamide (**1**) as well as a novel organotin(IV) complex (**2**) were synthesized and characterized by $^{1}H$, $^{13}C$, $^{31}P$ NMR, IR spectroscopy and elemental analysis. Also, the structures of compounds **1** and **2** were determined by X-ray crystallography. Using ultrasonic method, the nanoparticles of compounds **1** and **2** were prepared and investigated by SEM and XRD analyses. Comparing the structures **1** and **2** with those of reported phosphoramides (including nitrophenyl moiety in their structures) that have indicated potential therapeutical anticancer and enzyme-inhibitor properties [4,30,31] and with organotin(IV) complexes of phosphoramides possessing antibacterial activities [23], it can be expected that our new compounds will show desirable pharmaceutical applications.

## 2. Experimental

### 2.1. Instrumentation

The $^{1}H$, $^{13}C$, $^{31}P$ and $^{119}Sn$ spectra were recorded on a Bruker Avance DRS 500 spectrometer. $^{1}H$ and $^{13}C$ chemical shifts were determined relative to internal $Si(CH_3)_4$ and $^{31}P$ chemical shifts relative to 85% $H_3PO_4$ as external standard. Infrared (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.

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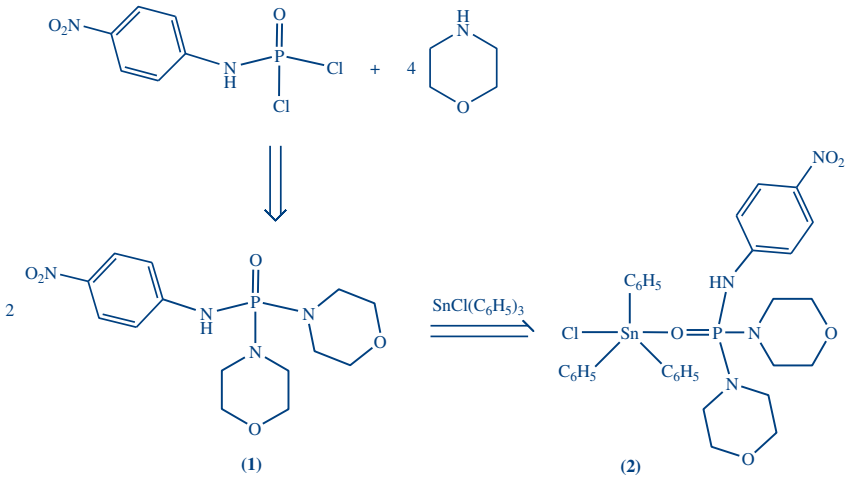


**Scheme 1.** The synthesis pathway of compounds **1** and **2**.

**Table 1**
Selected spectroscopic NMR and IR data of compounds **A**, **1** and **2**.

| Compound | $\delta(^{31}P)$ (ppm) | $^{2}J$(PNH) (Hz) | $^{3}J$(P,C) (Hz) | $\nu$(P=O) ($cm^{-1}$) | $\nu$(P–N) ($cm^{-1}$) | $\nu$(NH) ($cm^{-1}$) |
|---|---|---|---|---|---|---|
| 4-$NO_2C_6H_4NHP(O)Cl_2$ (**A**) | 6.34 | 10.6 | 9.0 | 1249 | 942 | 3400 |
| **1** | 9.99 | – | 7.0 (aromatic), 5.7 (aliphatic) | 1196 | 1104, 964 | 3425 |
| **2** | 10.30 | – | 6.6 (aromatic), 5.4 (aliphatic) | 1169 | 1111, 971 | 3445 |

The scanning electron microscopy (SEM) micrographs were obtained from Philips instrument (XL30), under vacuum, accelerated at 20 KV. The ultrasonic bath (Sono Swiss, model SW 12H with 50/60 Hz frequency, 1000 W power and 220–240 V voltage) was used for the synthesis of nanoparticles.

### 2.2. X-ray structure analysis

X-ray data of compounds **1** and **2** were collected at 120 K on a single crystal diffractometer Gemini with mirrors-collimated Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). The data processing including the empirical absorption correction by spherical harmonics was done with Crysalis Pro [32]. Structures were solved by the charge flipping algorithm of Superflip [33] and refined by Jana2006 [34]. The H-atom parameters for both structures were derived from the parent carbon atoms. For **1** we found two symmetry independent molecules while in the case of **2** only one symmetry independent molecule exists. For **2** the disordered $C_4H_8ON$ morpholinyl rings were described by a rigid body in four positions. It should be noted that the disorder in **2** could not be avoided by lowering of the symmetry.

**Table 2**
Crystallographic data for compounds **1** and **2**.

| Compound | **1** | **2** |
|---|---|---|
| Chemical formula | $C_{28}H_{42}N_8O_{10}P_2$ | $C_{32}H_{36}ClN_4O_5PSn$ |
| $M_r$ | 712.6 | 741.8 |
| Crystal system, space group | Monoclinic, $P2_1/n$ | Monoclinic, $P2_1/n$ |
| Temperature (K) | 121 | 120 |
| $a, b, c$ (Å) | 9.5609 (2), 10.6061 (3), 33.5907 (11) | 8.9123 (2), 37.5953 (6), 10.2917 (2) |
| $\beta$ (°) | 96.663 (2) | 107.196 (2) |
| $V$ (Å$^3$) | 3383.22 (16) | 3294.20 (12) |
| $Z$ | 4 | 4 |
| Radiation type | Cu K$\alpha$ | Cu K$\alpha$ |
| $\mu$ ($mm^{-1}$) | 1.74 | 7.75 |
| Crystal size (mm) | 0.27 × 0.13 × 0.12 | 0.35 × 0.27 × 0.16 |
| Diffractometer | Xcalibur, Atlas, Gemini ultra diffractometer | Xcalibur, Atlas, Gemini ultra diffractometer |
| Absorption correction | Multi-scan, CrysAlis PRO, Agilent Technologies | Multi-scan, CrysAlis PRO, Agilent Technologies |
| $T_{min}$, $T_{max}$ | 0.935, 1 | 0.455, 1 |
| No. of measured, independent and observed [$I > 3\sigma(I)$] reflections | 19,355, 5948, 5075 | 54,522, 5830, 5344 |
| $R_{int}$ | 0.022 | 0.054 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.597 | 0.598 |
| $R[F^2 > 3\sigma(F^2)]$, $wR(F^2)$, S | 0.031, 0.045, 1.50 | 0.025, 0.070, 1.25 |
| No. of reflections | 5948 | 5830 |
| No. of parameters | 439 | 366 |
| No. of restraints | 1 | 1 |
| H-atom treatment | Constrained | Constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.21, −0.29 | 0.35, −0.43 |

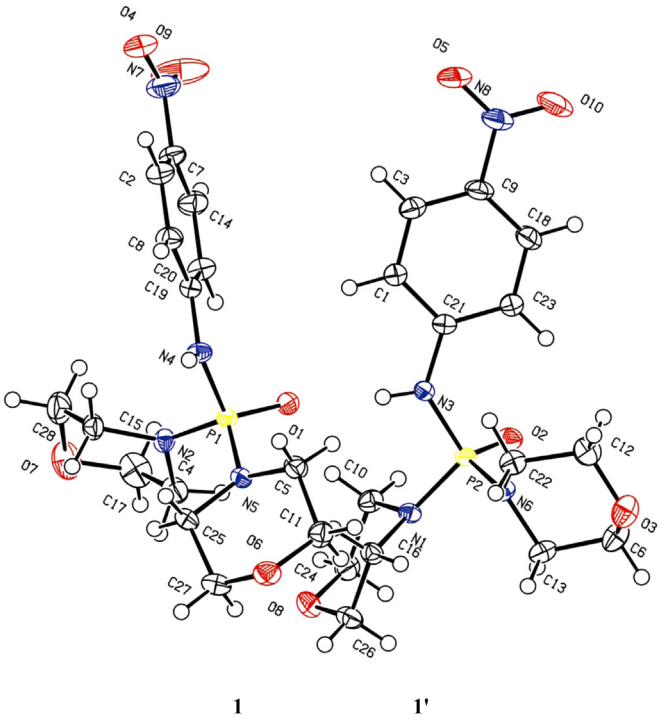


**Fig. 1.** The ORTEP view of the two independent molecules of compound **1** (50% probability ellipsoids).

### 2.3. Synthesis

#### 2.3.1. N-4-Nitrophenyl-N′,N″-bis(morpholinyl) phosphoric triamide (*1*)

To a solution of *N*-4-nitrophenyl phoramidic dichloride [35] (10 mmol, 2.55 g) in dry acetonitrile, morpholine (40 mmol, 3.48 g) was added dropwise at 0 °C and the mixture stirred for 24 h. Then the solution was evaporated and the yellow precipitate was filtered, washed with distilled water and recrystallized in MeOH/$CH_3CN$ mixture. Yield: 71%. M.p. = 194–195 °C. Anal. calcd. For $C_{14}H_{21}N_4O_5P$: C, 47.19; H, 5.94; N, 15.72. Found: C, 47.17; H, 5.95; N, 15.71%. $^{31}P$ NMR ($d_6$-DMSO): $\delta$ = 9.99 (m). $^1H$ NMR ($d_6$-DMSO): $\delta$ = 3.04 (m, 8H, $4CH_2$), 3.50 (m, 8H, $4CH_2$), 7.34 (d, $^3J$(H,H) = 9.1 Hz, 2H), 8.10 (d, $^3J$(H,H) = 9.1 Hz, 2H). $^{13}C$ NMR ($d_6$-DMSO): $\delta$ = 44.72 (s, $CH_2$), 66.87 (d, $^3J$(P,C) = 5.7 Hz, $CH_2$), 117.63 (d, $^3J(P,C_{ortho})$ = 7.0 Hz), 125.70 (s), 140.55 (s), 150.45 (s). IR (KBr): $\nu$ = 3425 (NH), 2835, 1589 ($NO_2$), 1512, 1485, 1341 ($NO_2$), 1297, 1252, 1196 (P=O), 1104 (P–N), 964 (P–N), 929, 842, 685, 526 $cm^{-1}$.

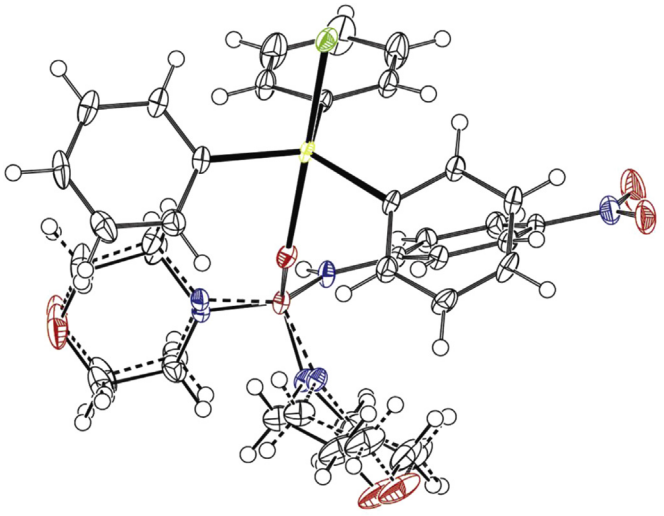

**Fig. 2.** The ORTEP view of compound **2** (50% probability ellipsoids).

**Table 3**
Selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

| **1** | | **2** | |
|---|---|---|---|
| P1–O1 | 1.4759 (11) | Sn1–Cl1 | 2.5340 (6) |
| P1–N2 | 1.6383 (12) | Sn1–C2 | 2.132 (2) |
| P1–N4 | 1.6569 (12) | Sn1–C6 | 2.123 (3) |
| P1–N5 | 1.6469 (12) | Cl1–$N1^i$ | 3.289 (2) |
| P2–O2 | 1.4761 (11) | P1–O1 | 1.4828 (18) |
| P2–N1 | 1.6451 (12) | P1–N1 | 1.651 (2) |
| P2–N3 | 1.6580 (12) | P1–N3a | 1.686 (7) |
| P2–N6 | 1.6341 (12) | P1–N3c | 1.635 (14) |
| O3–C6 | 1.4323 (18) | N1–C7 | 1.401 (3) |
| O3–C12 | 1.4307 (19) | N1–H1n1 | 0.87 (3) |
| N1–C10 | 1.4764 (18) | C2–C16 | 1.388 (3) |
| O1–P1–N2 | 111.52 (6) | Cl1–Sn1–C1 | 92.55 (6) |
| O1–P1–N4 | 113.49 (6) | Cl1–Sn1–C2 | 93.82 (6) |
| O1–P1–N5 | 111.14 (6) | Cl1–Sn1–C6 | 92.83 (6) |
| N2–P1–−N4 | 105.46 (6) | C1–Sn1–C2 | 124.57 (9) |
| N2–P1–N5 | 108.94 (6) | C1–Sn1–C6 | 119.49 (8) |
| N4–P1–N5 | 105.95 (6) | C2–Sn1–C6 | 115.09 (9) |
| O2–P2–N1 | 110.96 (6) | Sn1–Cl1–$N1^i$ | 114.93 (4) |
| O2–P2–N3 | 112.46 (6) | O1–P1–N1 | 113.22 (9) |
| O2–P2–N6 | 115.54 (6) | O1–P1–N3a | 107.9 (3) |
| N1–P2–N3 | 107.76 (6) | O1–P1–N3c | 111.9 (6) |
| N1–P2–N6 | 103.57 (6) | N1–P1–N3a | 104.9 (3) |
| N3–P2–N6 | 105.89 (6) | N1–P1–N3c | 107.7 (6) |
| P2–N1–C10 | 118.23 (9) | N3a–P1–N3c | 111.1 (5) |
| P2–N1–C16 | 122.57 (9) | $Cl1^{ii}$–N1–P1 | 121.38 (9) |
| C10–N1–C16 | 111.78 (11) | $Cl1^{ii}$–N1–C7 | 110.67 (15) |
| P1–N2–C4 | 120.00 (9) | $Cl1^{ii}$–N1–H1n1 | 6.2 (16) |
| P1–N2–C15 | 125.69 (9) | P1–N1–C7 | 127.95 (19) |
| C4–N2–C15 | 113.00 (11) | P1–N1–H1n1 | 115.3 (16) |
| P2–N3–C21 | 128.18 (10) | C7–N1–H1n1 | 116.8 (16) |
| P2–N3–H1n3 | 115.2 (11) | Sn1–C1–C4 | 118.49 (16) |
| C21–N3–H1n3 | 114.9 (12) | Sn1–C1–C10 | 123.09 (15) |
| C6–O3–C12 | 110.75 (11) | C4–C1–C10 | 118.3 (2) |

Symmetry code(s): (i) $x + 1, y, z$.; (ii) $x - 1, y, z$.

#### 2.3.2. [N-4-Nitrophenyl-N′,N″-bis(morpholinyl) phosphoric triamide] triphenyl stannate(IV) chloride (*2*)

To a solution of *N*-4-nitrophenyl-N′,N″-bis(morpholinyl) phosphoric triamide (10 mmol, 3.56 g) in methanol, triphenyltin(IV) chloride (10 mmol, 3.86 g) was added at room temperature and the solution was stirred for 72 h. Then the solution was slowly evaporated at RT to yield the single crystals. Yield: 51%. M.p. = 184–185 °C. Anal. Calc. For $C_{32}H_{36}ClN_4O_5PSn$: C, 51.84; H, 4.86; N, 7.55%. Found: C, 51.82; H, 4.85; N, 7.56%. $^{31}P\{^1H\}$ NMR ($d_6$-DMSO): $\delta$ = 10.30 (s). $^1H$ NMR ($d_6$-DMSO): $\delta$ = 3.25 (m, 8H, $CH_2$), 3.66 (m, 8H, $CH_2$), 7.25 (d, $^3J$(H,H) = 9.0 Hz, 2H, Ar–H), 7.51 (t, $^3J$(H,H) = 6.4 Hz, 8H, Ar–H), 7.70–7.77 (m, 7H, Ar–H), 8.17 (d, $^3J$(H,H) = 9.0 Hz, 2H, Ar–H). $^{13}C$ NMR ($d_6$-DMSO): $\delta$ = 44.85 (s), 66.99 (d, $^3J$(P,C) = 5.4 Hz), 117.14 (d, $^3J$(P,C) = 6.6 Hz), 125.61 (s), 129.11 (s), 130.42 (s), 136.09 (s), 137.70 (s), 141.75 (s), 147.38 (s). IR (KBr, $cm^{-1}$): 3445 (NH), 3226, 3058 (CH), 2967 (CH), 2853, 1598 ($NO_2$), 1511, 1341 ($NO_2$), 1253, 1169 (P=O), 1111 (P–N), 971 (P–N), 927, 850, 732, 692, 457.

## 3. Results and discussion

### 3.1. Spectroscopic study

In this study, a new phosphoric triamide 4-$NO_2C_6H_4NHP(O)(NC_4H_8O)_2$ (**1**) and its organotin(IV) complex $SnCl(C_6H_5)_3$[4-$NO_2$

**Table 4**
Selected structural data for compounds **1**–**7**.

| Compound | Crystal system, space group | P=O/P=S | P–$N_{(nitroaniline)}$ | O–$PN_{(nitroaniline)}$/S–P–$N_{(nitroaniline)}$ | P–$N_{(nitroaniline)}$–C | Ref |
|---|---|---|---|---|---|---|
| 4-$NO_2C_6H_4NHP(O)(NC_4H_8O)_2$ (**1**) | Monoclinic, $P2_1/n$ | 1.476 (1), 1.476 (1) | 1.657 (1), 1.658 (1) | 113.49 (6), 112.46 (6) | 127.3 (1), 128.2 (1) | [b] |
| $SnCl(C_6H_5)_3L_2$ (**2**)[a] | Monoclinic, $P2_1/n$ | 1.483 (2) | 1.651 (2) | 113.22 (9) | 128.0 (2) | [b] |
| 4-$NO_2C_6H_4NHP(O)(OCH_3)_2$ (**3**) | Orthorhombic, Pbcn | 1.467 (2) | 1.639 (2) | 108.23 (8) | 128.8 (1) | [40] |
| 4-$NO_2C_6H_4NHP(O)(4\text{-}CH_3\text{-}NC_5H_9)_2$ (**4**) | Monoclinic, $P2_1/c$ | 1.479 (1) | 1.661 (2) | 113.43 (8) | 127.4 (1) | [41] |
| 4-$NO_2C_6H_4NHP(O)(OCH_3)_2$ (**5**) | Orthorhombic, Pbcn | 1.462 (5) | 1.643 (7) | 109.4 (4) | 129.0 (6) | [42] |
| 4-$NO_2C_6H_4NHP(S)(OCH_2CH_3)_2$ (**6**) | Triclinic, $P\bar{1}$ | 1.911 (2) | 1.654 (3) | 110.3 (l) | 129.7 (3) | [43] |
| $PdCl_2L^1{}_2$ (**7**)[c] | Monoclinic, $P2_1/c$ | 1.972 (2) | 1.625 (3) | 110.0 (1) | 127.5 (2) | [43] |

[a] 4-$NO_2C_6H_4NHP(O)(NC_4H_8O)_2$ = L.
[b] This work.
[c] 4-$NO_2C_6H_4NHP(S)(OCH_2CH_3)_2$ = $L^1$.

$C_6H_4NHP(O)(NC_4H_8O)_2$] (**2**) were synthesized (Scheme 1) and characterized by NMR and IR spectroscopy. A summary of the spectroscopic parameters of these compounds and **A** [35] are given in Table 1. The phosphorus chemical shift, $\delta(^{31}P)$, appears at down field from compound **A** to **1** and **2** so that the $\delta(^{31}P)$ is the most down fielded in **2** (10.30 ppm). This down field shift shows the most electron withdrawing of substituents on the phosphorus atom in **2** results in a most deshielded phosphorus atom.

The $^1H$ NMR spectrum of compound **A** reveals $^2J$(PNH) coupling constant equal to 10.6 Hz while it disappears in the spectra of **1** and **2**. The $^{13}C$ NMR spectra indicate that $^3J(P,C_{aromatic})$ coupling constant decreases from 9.0 Hz (in **A**) to 6.6 Hz (in **2**). Also, $^3J(P,C_{aliphatic})$ coupling constant for the splitting of morpholinyl ring carbon atom with phosphorus reduces from 5.7 Hz (in **1**) to 5.4 Hz (in **2**). The reductions in $^3J$(P,C) coupling constants are due to the less interaction of carbon atoms with phosphorus atoms that are because of changes in electronic and spatial properties.

The IR spectra indicate that among these compounds, the $\nu$(P=O) value decreases from **A** (1249 $cm^{-1}$) to **2** (1169 $cm^{-1}$) exhibiting the weakening of the P=O bond. The $\nu$(P–N) increases from 942 $cm^{-1}$ (in **A**) to 971 $cm^{-1}$ (in **2**) that is due to the enhanced interaction of phosphorus atom with nitrogen lone pair to form a stronger partial multiple bond. Also, the NH stretching frequencies are observed at about 3400 $cm^{-1}$.

### 3.2. X-ray crystallography

Single crystals of compounds **1** and **2** were obtained by slow evaporation of the solvents at room temperature. The crystallographic data and the details of the X-ray analysis are presented in Table 2. Both compounds crystallize in the monoclinic crystal system with $P2_1/n$ space group. Phosphoramide **1** has two symmetrically independent molecules (**1** and **1′**) in the crystalline lattice (Fig. 1). The molecules are significantly different as manifested by

**Table 5**
The hydrogen bonding data of compounds **1** and **2** (Å, °).

| Compound | D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | D–H···A (°) |
|---|---|---|---|---|---|
| **1**[a] | N3–H1n3···O1 | 0.842 (17) | 1.910 (17) | 2.7490 (16) | 174.7 (17) |
| | N4–H1n4···O2$^{ii}$ | 0.842 (17) | 1.947 (17) | 2.7850 (16) | 174.0 (16) |
| | C2–H1c2···O4 | 0.96 | 2.44 | 2.728 (2) | 96.77 |
| | C3–H1c3···O5 | 0.96 | 2.45 | 2.7348 (19) | 96.80 |
| | C14–H1c14···O9 | 0.96 | 2.41 | 2.709 (2) | 97.61 |
| | C18–H1c18···O10 | 0.96 | 2.43 | 2.718 (2) | 97.03 |
| | C24–H1c24···O3$^{i}$ | 0.96 | 2.44 | 3.3895 (18) | 172.40 |
| **2**[b] | N1–H1n1···Cl1$^{i}$ | 0.87 (3) | 2.43 (3) | 3.289 (2) | 172 (2) |
| | C8–H1c8···O2 | 0.96 | 2.43 | 2.721 (3) | 96.80 |
| | C12–H1c12···O3 | 0.96 | 2.42 | 2.710 (3) | 97.24 |

[a] Symmetry code(s): (i) $x, y-1, z$; (ii) $x+1, y, z$.
[b] Symmetry code(s): (i) $x-1, y, z$.

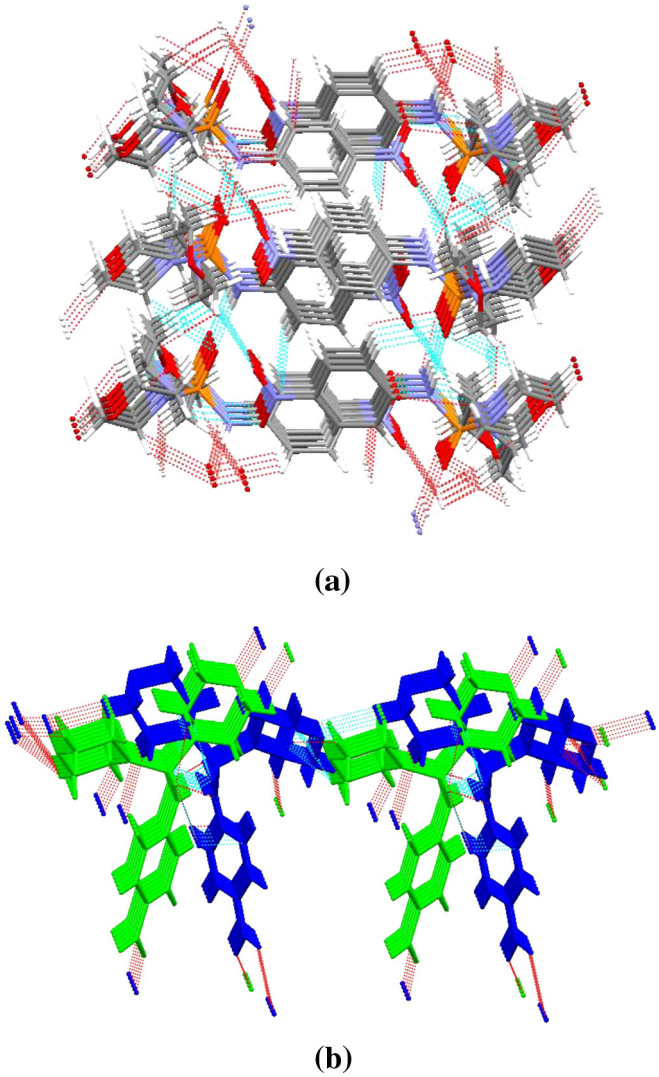


**Fig. 3.** The three-dimensional polymeric chain formed by hydrogen bonds in the crystal structure of **1**. Different colors denote chemical types in (a) and different molecules in (b).

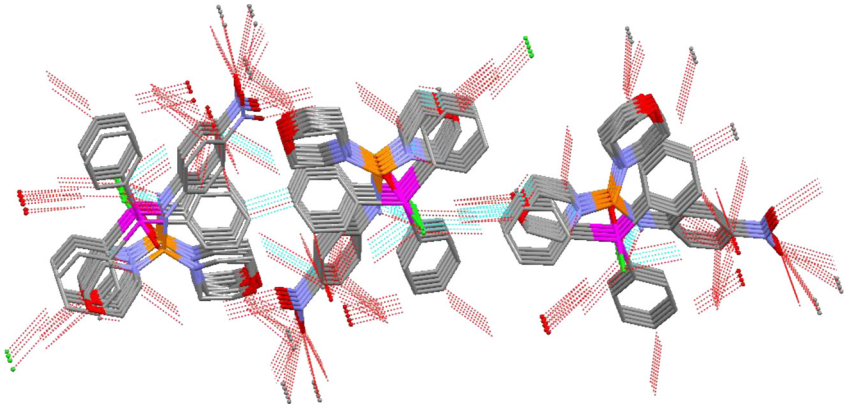

**Fig. 4.** The three-dimensional polymeric chain formed by hydrogen bonds in the crystal structure of **2**.

their torsion angles. For instance, the O1–P1–N4–C19, O2–P2–N3–C21 and N2–P1–N4–C19, N1–P2–N3–C21 torsion angles are 46.75°, −30.69° and −75.60°, −153.30°, respectively.

The ORTEP view of complex **2** is represented in Fig. 2. In **2**, all of the endocyclic atoms of morpholinyl rings reveal disorder. In the structure refinement the disorder was sufficiently described by one morpholinyl ring in a chair conformation which was placed to four positions. Selected bond lengths and angles of compounds **1** and **2** are given in Table 3. The P=O bond lengths in molecules **1**, **1′** and **2** are 1.4759 (11) Å, 1.4761 (11) Å and 1.4828 (18) Å that are larger than the normal P=O bond length (1.45 Å) [36]. It is seen that the P=O bond length is longer in complex **2** relative to those of **1** and **1′** that is due to its weakening upon complexation via phosphoryl oxygen atom. The central Sn atom in **2** has a distorted trigonal bipyramidal configuration in which three phenyl rings are placed at equatorial positions while the Cl atom and phosphoric triamide ligand are in axial positions (with Cl–Sn–O bond angle = 176.16°).

The P atoms have slightly distorted tetrahedral configurations with the surrounding angles around the P atoms in the range of 105.46 (6)° – 113.49 (6)°, 103.57 (6)° – 115.54 (6)° and 104.9 (3)° – 113.22 (9)° for molecules **1**, **1′** and **2**, respectively. The P–N bonds are shorter than the typical P–N single bond length (1.77 Å) [36]. The environments of nitrogen atoms bonded to the morpholinyl ring in a chair conformation are deviated from planarity. In compound **1**, the angles P1–N2–C4, P1–N2–C15 and C4–N2–C15 are 120.00 (9)°, 125.69 (9)°, 113.00 (11)°, respectively, with average 119.56°. Also, the sums of surrounding angles around exocyclic N4 and endocyclic N5 atoms in **1** are 360.06° and 351.94°, respectively, indicating a planar configuration for N4 and a distorted planar configuration for N5. Analogous observations can be found for the nitrogen atoms in molecules **1′** and **2**. The Sn–C bond lengths in **2** are 2.132 (2), 2.123 (3) and 2.135 Å that are close to those reported in the literature [37]. The Sn–Cl bond length is 2.5340 (6) Å lying near to the normal covalent radii 2.37–2.60 Å [38]. The Sn–O bond length is 2.313 Å that is shorter than sum of the van der Waals radii of Sn and O atoms (3.70 Å) [39].

Selected structural data for compounds **1**, **2** and for similar compounds **3**–**7** all containing 4-nitroaniline group [40–43] are

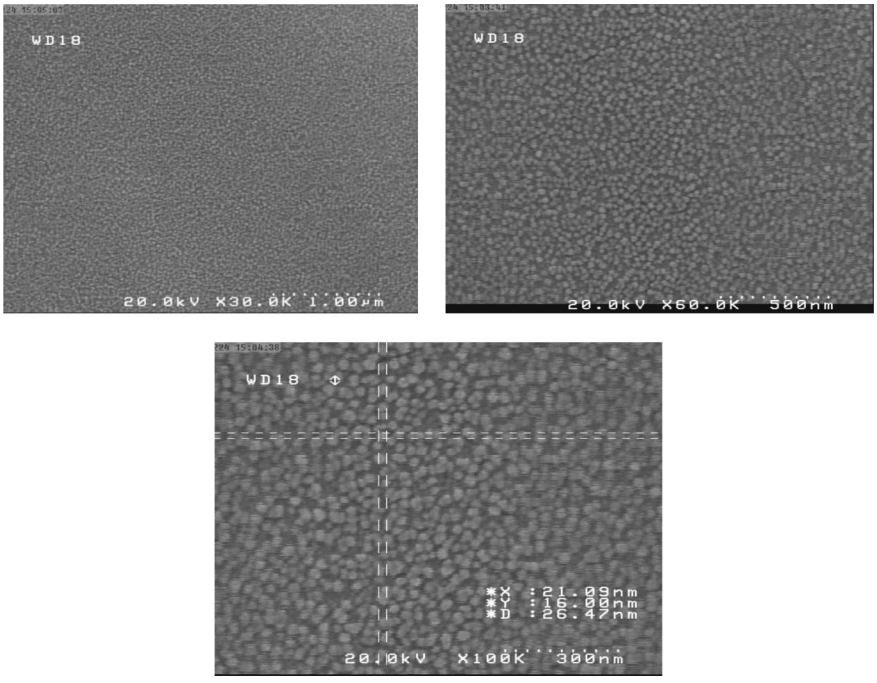


**Fig. 5.** The SEM micrographs of compound **1** with 30k, 60k and 100k magnifications.

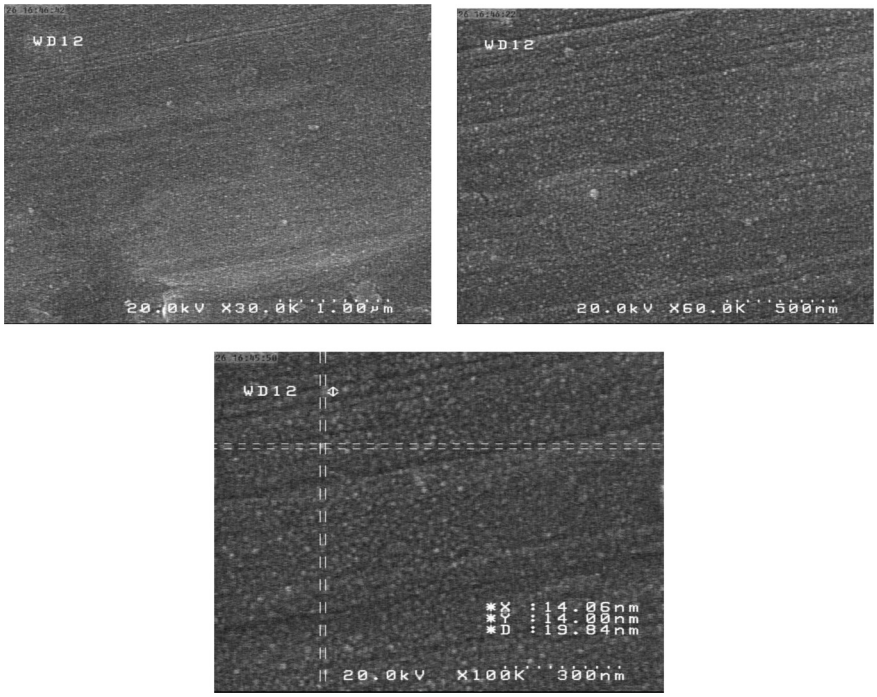


**Fig. 6.** The SEM micrographs of compound **2** with 30k, 60k and 100k magnifications.

presented in Table 4. It is seen from the table that the P═O, P═S and P–$N_{(nitroaniline)}$ bond lengths are in the range of 1.462 (5)° – 1.483 (2)°, 1.911 (2)° – 1.972 (2)° and 1.625 (3)° – 1.661 (2)°, respectively. The O–P–$N_{(nitroaniline)}$ and S–P–$N_{(nitroaniline)}$ bond angles are nearly tetrahedral that range from 108.23 (8)° to 113.49 (6)° while P–$N_{(nitroaniline)}$–C bond angles are almost planar and range from 127.3 (1)° to 129.7 (3)°. In all compounds **1**–**7**, the phosphorus atoms reveal slightly distorted tetrahedral configurations. Also, strong intermolecular N–H···O═P hydrogen bonds are observed in these structures.

The details about hydrogen bonding of compounds **1** and **2** are given in Table 5. In compound **1**, the two symmetrically independent molecules are connected to each other through alternating intermolecular strong N3–H1n3···O1 and N4–H1n4···O2 hydrogen bonds to form a one dimensional polymeric chain. Besides, weak intermolecular C–H···O hydrogen bonds generate a 3-D polymeric chain in the crystal structure (Fig. 3). In complex **2**, the N1–H1n1···Cl1 strong intermolecular hydrogen bonds produce a 1-D polymeric chain, which is completed in a 3-D network by weak intermolecular C–H·O hydrogen bonds (Fig. 4).

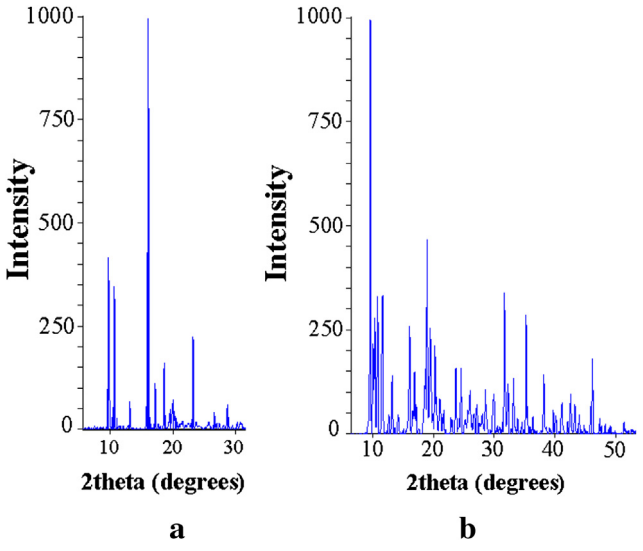


**Fig. 7.** The XRD patterns of the nanoform of the compounds **1** (a) and **2** (b).

### 3.3. Nanoparticle preparation

Nowadays, many chemists employ the ultrasonic method for the synthesis of nanoscale organic/inorganic compounds [44–46]. The apparent advantage of this technique lies in a straightforward methodology and possibility to use a relatively simple apparatus [47,48]. The nanoparticles of compounds **1**, **2** were prepared by performing the synthesis in an ultrasonic bath at 30 °C for about 1 h. It is notable that nanoparticles can be obtained from both dissolved and powdered samples. For the dissolved samples, some droplets of them are placed on a small piece of foil while the powdered compounds are directly placed on the sample holder for taking the SEM images. Here, the complexes were dissolved in methanol and after evaporation of the solvent, the SEM images were obtained from the nanoparticles prepared on aluminum foil.

The SEM micrographs shown in Figs. 5 and 6 indicate the particle sizes are about 15–20 nm with an identical spherical morphology. The XRD patterns in Fig. 7 indicate sharp peaks due to high crystallinity with the sharpest peaks for compounds **1**, **2** appear at 2$\theta$ values of 15.9° and 9.5°, respectively. Using Debye–Scherrer equation [49], the crystal sizes of compounds **1**, **2** were estimated from the XRD diagrams about 38.10 and 69.23 nm, respectively.

## 4. Conclusions

The synthesis, X-ray crystallography and nanoparticle preparation of a new phosphoric triamide (**1**) and an organotin(IV) complex (**2**) were performed. Compound **1** revealed two symmetrically independent molecules in the crystal lattice and compound **2** showed

a distorted trigonal bipyramidal configuration for the central tin(IV) atom. In both compounds, the strong intermolecular N–H···O and N–H···Cl hydrogen bonds plus weak intermolecular C–H···O hydrogen bonds formed 3-D polymeric structures Scheme 1.

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## Appendix A. Supplementary material

CCDC 942194 and 937436 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## References

[1] A.-L. Villard, G. Coussot, I. Lefebvre, P. Augustijns, A.-M. Aubertin, G. Gosselin, S. Peyrottes, C. Perigaud, Bioorg. Med. Chem. 16 (2008) 7321–7329.
[2] C. McGuigan, F. Daverio, I. Nájera, J.A. Martin, K. Klumpp, D.B. Smith, Bioorg. Med. Chem. Lett. 19 (2009) 3122–3124.
[3] C. McGuigan, M.R. Kelleher, P. Perrone, S. Mulready, G. Luoni, F. Daverio, S. Rajyaguru, S. Le Pogam, I. Najera, J.A. Martin, K. Klumpp, D.B. Smith, Bioorg. Med. Chem. Lett. 19 (2009) 4250–4254.
[4] L. Hu, C. Yu, Y. Jiang, J. Han, Z. Li, P. Browne, P.R. Race, R.J. Knox, P.F. Searle, E.I. Hyde, J. Med. Chem. 46 (2003) 4818–4821.
[5] R.J. Hansen, S.M. Ludeman, S.J. Paikoff, A.E. Pegg, M.E. Dolan, DNA Repair 6 (2007) 1145–1154.
[6] M. Jain, J. Fan, N.Z. Baturay, C.-H. Kwon, J. Med. Chem. 47 (2004) 3843–3852.
[7] M.J. Domínguez, C. Sanmartín, M. Font, J.A. Palop, S. San Francisco, O. Urrutia, F. Houdusse, J.M. García-Mina, J. Agric. Food Chem. 56 (2008) 3721–3731.
[8] M. Hatano, T. Miyamoto, K. Ishihara, Org. Lett. 9 (2007) 4535–4538.
[9] D.-M. Du, T. Fang, J. Xu, S.-W. Zhang, Org. Lett. 8 (2006) 1327–1330.
[10] Z. Shariatinia, E. Asadi, M. Yousefi, M. Sohrabi, J. Organomet. Chem. 715 (2012) 82–92.
[11] K. Gholivand, Z. Shariatinia, M. Pourayoubi, Z. Naturforsch. 60b (2005) 67–74.
[12] K. Gholivand, Z. Hosseini, M. Pourayoubi, Z. Shariatinia, Z. Anorg. Allg. Chem. 631 (2005) 3074–3079.
[13] K. Gholivand, C.O.D. Vedova, A.A. Firooz, A. Madani Alizadehgan, M.C. Michelini, R. Pis Diez, J. Mol. Struct. 750 (2005) 64–71.
[14] K. Gholivand, Z. Shariatinia, M. Pourayoubi, Polyhedron 25 (2006) 711–721.
[15] K. Gholivand, Z. Shariatinia, J. Organomet. Chem. 691 (2006) 4215–4224.
[16] C. Zhu, L. Yang, D. Li, Q. Zhang, J. Dou, D. Wang, Inorg. Chim. Acta 375 (2011) 150–157.
[17] B. Gleeson, J. Claffey, D. Ertler, M. Hogan, H. Müller-Bunz, F. Paradisi, D. Wallis, M. Tacke, Polyhedron 27 (2008) 3619–3624.
[18] C.J. Cardin, A. Roy, Inorg. Chim. Acta 107 (1985) 57–61.
[19] R. Singh, N.K. Kaushik, Spectrochim. Acta Part A 71 (2008) 669–675.
[20] A.K. Mishra, N. Manav, N.K. Kaushik, Spectrochim. Acta Part A 61 (2005) 3097–3101.
[21] J. Otera, T. Yano, E. Kunimoto, T. Nakata, Organometallics 3 (1984) 426–431.
[22] K. Gholivand, N. Oroujzadeh, F. Afshar, J. Organomet. Chem. 695 (2010) 1383–1391.
[23] K. Gholivand, S. Farshadian, Z. Hosseini, K. Khajeh, N. Akbari, Appl. Organomet. Chem. 24 (2010) 700–707.
[24] Solomon Assefa, Fengnian Xia, Yurii A. Vlasov, Nature 464 (7285) (2010) 80–84.
[25] N. Melosh, A. Boukai, F. Diana, B. Gerardot, A. Badolato, P. Petroff, J.R. Heath, Science 300 (2003) 112–115.
[26] J. Xiang, W. Lu, Y. Hu, Y. Hao, Y. Wu, C.M. Lieber, Nature 441 (2006) 489–493.
[27] I.R. Corbin, K.K. Ng, L. Ding, A. Jurisicova, G. Zheng, Nanomedicine 8 (2013) 875–890.
[28] J. Zhong, S. Yang, X. Zheng, T. Zhou, D. Xing, Nanomedicine 8 (2013) 903–919.
[29] Z. Shariatinia, E. Asadi, V. Tavasolinasab, K. Gholivand, Beilstein J. Nanotechnol. 4 (2013) 94–102.
[30] R. Reinhard, B.F. Schmidt, J. Org. Chem. 63 (1998) 2434–2441.
[31] Y. Jiang, L. Hu, Bioorg. Med. Chem. Lett. 18 (2008) 4059–4063.
[32] Agilent Technologies CrysAlis PRO, 2010. Yarnton, Oxfordshire, UK.
[33] L. Palatinus, G. Chapuis, J. Appl. Crystallogr. 40 (2007) 786–790.
[34] V. Petricek, M. Dusek, L. Palatinus, Jana2006. Structure Determination Software Programs, Institute of Physics, Praha, Czech Republic, 2006.
[35] K. Gholivand, Z. Shariatinia, Z. Ahmadian Tabasi, A. Tadjarodi, Heteroat. Chem. 17 (2006) 337–343.
[36] D.E.C. Corbridge, Phosphorus, an Outline of its Chemistry, Biochemistry and Technology, fifth ed., Elsevier, The Netherlands, 1995.
[37] C.L. Ma, F. Li, Q. Jiang, R.F. Zhang, J. Organomet. Chem. 689 (2004) 96–104.
[38] F.H. Allen, S.A. Bellard, M.D. Brice, B.A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B.G. Hummelink-Peters, O. Kennard, W.D.S. Motherwell, J.R. Rogers, D.G. Watson, Acta Crystallogr. B35 (1979) 2331–2339.
[39] J. Beckmann, M. Henn, K. Jurkschat, M. Schürmann, D. Dakterniek, A. Duthie, Organometallics 21 (2002) 192–202.
[40] K. Gholivand, Z. Shariatinia, M. Pourayoubi, Z. Kristallogr. NCS 220 (2005) 65–66.
[41] K. Gholivand, Z. Shariatinia, M. Pourayoubi, Z. Anorg. Allg. Chem. 631 (2005) 961–967.
[42] M.P. Du Plessis, T.A. Modro, L.R. Nassimbeni, Acta Crystallogr. B38 (1982) 1504–1507.
[43] J.R. Phillips, D.J. Williams, A.M.Z. Slawin, J.D. Woolins, Polyhedron 15 (1996) 3725–3729.
[44] B.P. Baranwal, T. Fatma, A.K. Singh, A. Varma, Inorg. Chim. Acta 362 (2009) 3461–3464.
[45] Y. Lv, J. Zhang, W. Cao, Y. Fu, Spectrochim. Acta Part A 72 (2009) 22–25.
[46] M. Zhou, Q. He, J. Rare Earths 26 (2008) 473–477.
[47] C.E. Domini, G.F. Silbestri, B.F. Band, A.B. Chopa, Ultrason. Sonochem. 19 (2012) 410–414.
[48] P. Banerjee, S. Chakrabarti, S. Maitra, B.K. Dutta, Ultrason. Sonochem. 19 (2012) 85–93.
[49] A. Patterson, Phys. Rev. 56 (1939) 978–982.