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New organotin(IV) complexes of nicotinamide, isonicotinamide and some of their novel phosphoric triamide derivatives: Syntheses, spectroscopic study and crystal structures

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ABSTRACT

Three novel phosphoramidate ligands with formula $RP(O)R'_2$, R = Nicotinamide(nia), R′ = $NHC(CH_3)_3$(**L_1**), $NH(C_6H_{11})$ (**L_2**); R = isonicotinamide(iso), $NH(C_6H_{11})$ (**L_3**) and their new organotin(IV) complexes with formula $SnCl_2(CH_3)_2(X)_2$, X = L_1 (**C_1**), L_2 (**C_2**), L_3 (**C_3**) plus $SnCl_2(CH_3)_2(L_4)_2$(**C_4**), **L_4** = $isoP(O)[NHC(CH_3)_3]_2$, were synthesized and characterized by ^1H, ^{13}C, ^{31}P,^{119}Sn NMR, IR, UV–Vis spectroscopy and elemental analysis. Two novel complexes of nia and iso with formula $SnCl_2(CH_3)_2(X)_2$, X = nia (**C_5**), iso (**C_6**) were also prepared and all the complexes were spectroscopically studied in comparison to their related ligands and to each other. The crystal structure of complexes **C_1**, **C_3**, **C_4**, and **C_5** were determined by X-ray crystallography. –Sn–Cl···H–N– major hydrogen bonds beside other electrostatic interactions produced a three dimensional polymeric cluster in the crystalline lattice of **C_1**, **C_3**, **C_5** and a two dimensional polymeric chain in **C_4**. Results showed that coordination of the phosphoramidate ligand (**L_4**) to Sn in **C_4** has been occurred from the nitrogen site of the pyridine ring similar to **C_5**, **C_6** in which there is no P═O donor site; however, in **C_1** and **C_3** the active donor site of corresponding ligands is P═O. It seems that in these complexes there is a competition between P═O and $N_{pyridine}$ donor sites and the influential factor which determines the winner site is the type of substituents on phosphorus atom.

1. Introduction

Nicotinamide (known also as vitamin PP, pellagra protective, vitamin B3, etc.) and isonicotinamide are two pyridine type ligands (see Fig. 1) with wide range of chemical and biological applications [1–3].

Nicotinamide is a part of the pyridine nucleotides as NADC and NADPC that plays a crucial role in biological oxidative chemistry and is essential for the human body [1,2]. Isonicotinamide possesses strong antitubercular, antipyretic, fibrinolytic and antibacterial properties. The mixed salts of this amide have extensive uses as drugs in various biological and medicinal processes [3]. Although numerous derivatives of nicotin- and isonicotinamide have been reported in the literature we could not find any phosphoramidate containing these amides. Phosphoramidates including –C(O)N(H)-P(O)– moiety have been used as O-donor ligands in the reaction with various metal ions up to now [4–15]. The presence of a peptide group in these compounds causes its diverse biological activity and used as anticancer drugs [16]. With respect to these important points about phosphoramidates, following to our previous works [17,18], we attempted to synthesize new phosphoramidates, including nicotinamide and isonicotinamide. In addition, since metal complexes of biologically important ligands are sometimes more effective than the free ligands [19] we also focused on complexation of nicotinamide, isonicotinamide and their new phosphoramidates (prepared in this work) with Sn metal. Although various complexes of these two amides (nia, iso) have been studied with several metals such as Mn, Co, Cu, Ni, Zn, Ag, Mg, Pb, Rh [20–25], to the best of our knowledge no organotin complexes of these types of ligands have been reported in literature. Organotin complexes have been studied by various methods in last four decades. Much of the interest in such complexes arises from their catalytic and biological activity [26] and their applications as fungicides or antifouling agents, antitumor and antimicrobial compounds [27–29].

In this work three novel phosphoramidate ligands with formula $RP(O)R'_2$, R = Nicotinamide(nia), R′ = $NHC(CH_3)_3$(**L_1**), $NH(C_6H_{11})$ (**L_2**), R = isonicotinamide(iso), $NH(C_6H_{11})$ (**L_3**); plus R = (iso), R′ = $NHC(CH_3)_3$ (**L_4**, reported in previous work [18]) were synthesized and spectrally studied in comparison to their new complexes with formula $SnCl_2(CH_3)_2(X)_2$, X = L_1 (**C_1**), L_2 (**C_2**), L_3 (**C_3**), L_4 (**C_4**). Furthermore two new organotin complexes with formula $SnCl_2(CH_3)_2(X)_2$, X = nia (**C_5**), iso (**C_6**) were prepared and the crystal structure of

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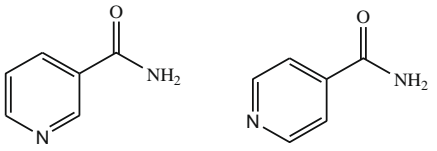

Nicotinamide(nia) Isonicotinamide(iso)

Fig. 1. Molecular view of nicotinamide and isonicotiamide.

complexes **C₁**, **C₃**, **C₄**, **C₅** were determined by X-ray crystallography. The characterization studies were carried out by ^{1}H, ^{13}C, ^{31}P, ^{119}Sn NMR, IR, UV spectroscopy and elemental analysis.

2. Materials and methods

2.1. X-ray measurements

X-ray data of compounds **C₁**, **C₄** were collected on a Bruker APEX-II CCD [56] and for compound **C₃**, **C₅** on a Bruker SMART 1000 CCD [57] area detector with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were refined with SHELXTL (for **C₁**, **C₃**, **C₅**) [58] and SHELXL-97(for **C₄**) [59] by full-matrix least-squares on F^2. The positions of hydrogen atoms were obtained from the difference Fourier map. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program for compounds **C₁**, **C₃**, **C₄**, **C₅** [60].

2.2. Spectroscopic measurements

^{1}H, ^{13}C, ^{31}P and ^{119}Sn NMR spectra were recorded on a FT-NMR, Bruker Avance DRS 500 spectrometer. ^{1}H and ^{13}C chemical shifts were determined relative to TMS. ^{31}P and ^{119}Sn chemical shifts were measured relative to 85% H_3PO_4 and $Sn(CH_3)_4$ as external standards respectively. Infrared (IR and FTIR) spectra were recorded on a Shimadzu model IR-60 and FTIR (Thermo Nicolet) Nexus 870 spectrometers. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus.

2.3. Syntheses

After refluxing of phosphorus pentachloride and nicotinamide ($C_5H_4NC(O)NH_2$) in 1:1 molar ratio in CCl_4 for 6 h, solution let to get cold to the room temperature. Then formic acid was syringed drop-wise into the vigorously stirring solution in 15 min and let to stir for 6 h. Resulting white precipitate A, was filtered and dried. Precipitate B, was also prepared from the reaction of phosphorus pentachloride with Isonicotinamide exactly similar to the procedure used to produce A.

2.3.1. N-nicotinyl, N′,N″-bis(tert-butyl) phosphoric triamide

2.3.1.1. $C_5H_4NC(O)NHP(O)[NHC(CH_3)_3]_2$ (***L₁***). Compound **L₁** was synthesized from the reaction of precipitate A with *t*-butyl amine in 1:4 molar ratio of nicotinamide (initiator): corresponding amine. The mentioned amine was added drop-wise to a mixture of reaction in acetonitrile (40 mL) while stirring. The temperature was not allowed to rise above 4 °C. After stirring for 8 h and then evaporating the solvent, the residue was washed with distilled H_2O.

Yield (mol): 72%. Elemental Anal. Calc. for: C, 53.85; H, 8.01; N, 17.95. Found: C, 53.70; H, 8.03; N, 17.99%. IR (KBr, cm^{-1}): $\bar{\nu}$ = 3320(m, NH), 3120(m), 2950(m, CH_2), 1636(vs, C═O), 1584(m, ν_{ring}), 1441(s, δ_{CH}), 1405(s), 1287(m, ν_{ring}), 1237(s, P═O), 1205(s), 1117(w), 1014(s, ν_{ring}), 886(m), 850(w), 803(m), 730(m), 584(m), 530(m), 488(w). ^{1}H NMR (500.13 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 1.21(m, 18H), 4.06(d, ^{2}J(PNH) = 7.1 Hz, 2H, NH_{amine}), 7.47(dd, ^{3}J(H,H) = 7.8 Hz, ^{3}J(H,H) = 4.8 Hz, 1H), 8.29(d, ^{3}J(H,H) = 7.9 Hz, 1H), 8.70(d, ^{3}J(H,H) = 4.7 Hz, 1H), 9.07(d, ^{5}J(P,H) = 2.1 Hz, 1H), 9.72(s, 1H, NH_{amide}). ^{13}CNMR (125.76 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 31.16(d, ^{3}J(P,C) = 4.9 Hz), 50.35(s), 123.25(s), 129.70(d, ^{3}J(P,C) = 7.9 Hz, C_{ipso}), 135.49(s), 149.02(s), 152.23(s), 166.77(s, C═O). ^{31}P NMR (202.46 MHz, d_6-DMSO, 25 °C, H_3PO_4 external) (ppm): δ = 3.66 (m). UV–Vis in methanol: λ_{max} = 240 nm.

2.3.2. N-nicotinyl, N′,N″-bis(cyclohexyl) phosphoric triamide

2.3.2.1. $C_5H_4NC(O)NHP(O)[NH(C_6H_{11})]_2$ (***L₂***). Compound **L₂** was synthesized and purified in the same way that was used for **L₂**, using cyclohexylamine instead of *t*-butyl amine.

Yield (mol): 89%. Elemental Anal. Calc. for: C, 59.34; H, 7.97; N, 15.38. Found: C, 59.19; H, 7.99; N, 15.42%. FTIR (KBr, cm^{-1}): $\bar{\nu}$ = 3285(s, NH), 2925(s, CH_2), 2852(ms), 1644(s, C═O), 1587(ms, ν_{ring}), 1485(ms), 1455(m), 1423(s, δ_{CH}), 1343(mw), 1295(mw), 1279(m, ν_{ring}), 1215(ms, P = O), 1185(m), 1118(mw), 1096(s), 1024(mw), 1002(m), 929(mw), 912(m), 883(m), 842(mw), 790(m), 756(mw), 709(m), 688(mw), 618(mw), 569(m), 523(m), 482(mw), 438(w), 410(w). ^{1}H NMR (500.13 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 1.14(m, 10H), 1.45(d, ^{3}J(H,H) = 11.8 Hz, 2H), 1.60(m, 4H), 1.75(m, 4H), 2.94(m, 2H), 4.21(dd, ^{2}J(PNH) = 9.5 Hz, ^{3}J(H,H) = 9.2 Hz, 2H, NH_{amine}), 7.49(dd, ^{3}J(H,H) = 7.9 Hz, ^{3}J(H,H) = 4.8 Hz,1H), 8.27(d, ^{3}J(H,H) = 8.0 Hz, 1H), 8.71(dd, ^{3}J(H,H) = 4.0 Hz, ^{7}J(P,H) = 1.2 Hz,1H), 9.06(d, ^{5}J(P,H) = 1.5 Hz, 1H, Ha), 9.59(s, 1H, NH_{amide}). ^{13}C NMR (125.76 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 24.68(d, J(P,C) = 10.1 Hz), 25.07(s), 34.91(d, ^{3}J(P,C) = 4.0 Hz), 35.18(d, ^{3}J(P,C) = 6.1 Hz), 49.29(s), 123.32(s), 129.52(d, ^{3}J(P,C) = 7.7 Hz, C_{ipso}), 135.49(s), 148.95(s), 152.33(s), 166.60(s, C = O). ^{31}P NMR (202.46 MHz, d_6-DMSO, 25 °C, H_3PO_4 external) (ppm): δ = 7.08 (m). UV–Vis in methanol: λ_{max} = 259.5 nm.

2.3.3. N-isonicotinyl, N′,N″-bis(cyclohexyl) phosphoric triamide

2.3.3.1. $C_5H_4NC(O)NHP(O)[NH(C_6H_{11})]_2$ (***L₃***). A mixture of cyclohexyl amine, (2 mmol, 0.23 mL), and triethylamine, (2 mmol, 0.28 mL), was added drop-wise to a solution of precipitate B (0.239 g) in chloroform (35 mL) at 0 °C and stirred for 72 h. After evaporating the solvent, the residue was washed with distilled H_2O.

Yield (mol): 67%. Elemental Anal. Calc. for: C, 59.34; H, 7.97; N, 15.38. Found: C, 59.19; H, 7.99; N, 15.32%. FTIR (KBr, cm^{-1}): $\bar{\nu}$ = 3315(s), 3248(s), 2926, 2854(s), 1661(s, C═O), 1556(mw), 1496(mw), 1455(s), 1434(s), 1410(mw), 1271(mw), 1200(s, P═O), 1185(mw), 1110(s), 1071(w), 1068(w), 1002(w), 930(w), 915(mw), 884(mw), 798(mw), 791(mw), 759(mw), 681, 661(w), 579(w), 548(w), 518(w), 485(w)cm^{-1}. ^{1}H NMR (500.13 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 1.29(m, 10H), 1.46(d, ^{3}J(H,H) = 11.8 Hz, 2H), 1.60 (m, 4H), 1.74 (dd, ^{2}J(H,H) = 28.2 Hz, ^{4}J(P,H) = 2.4 Hz, 4H), 2.93(m, 2H), 2.22 (dd, ^{2}J(PNH) = 9.3 Hz, ^{3}J(H,H) = 9.5, 2H, NH_{amin}), 7.82 (dd, ^{3}J(H,H) = 5.9 Hz, ^{6}J(P,H) = 1.6 Hz, 2H), 8.71(m, 2H), 9.61(s, 1H, NH_{amide}). ^{13}C NMR (125.76 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 166.46(s, C═O), 150.14(s), 140.92 (d, ^{3}J(P,C) = 8.0 Hz), 121.47(s), 49.24(s), 35.14 (d, ^{3}J(P,C) = 6.1 Hz), 34.85 (d, ^{3}J(P,C) = 4.1 Hz), 25.03(s), 24.62(d, J(P,C) = 9.4 Hz). ^{31}P NMR (202.46 MHz, d_6-DMSO, 25 °C, H_3PO_4 external) (ppm):δ = 6.84 (m). UV–Vis in ethanol: λ_{max} = 201.8 nm.

2.3.4. N-isonicotinyl, N′,N″-bis(t-butyl) phosphoric triamide

2.3.4.1. $C_5H_4NC(O)NHP(O)[NHC(CH_3)_3]_2$ (***L₄***). This ligand was prepared as our previous reported pathway [18].

Yield (mol): 65%. Elemental Anal. Calc. for: C, 53.85; H, 8.01; N, 17.95. Found: C, 53.69; H, 8.03; N, 18.01%. FTIR (KBr, cm^{-1}):