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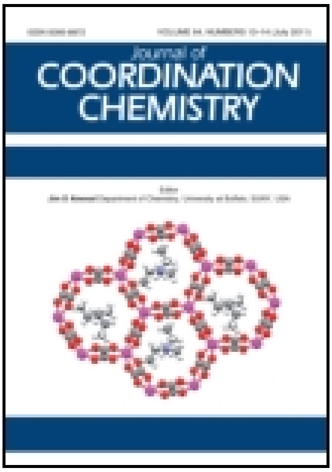

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Synthesis and characterization of a new cyclic phosph(V)azane ligand $[(C_6H_5N)P(O)H]_2$ and its zinc(II) complex

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The new cyclic phosph(V)azane ligand $[(C_6H_5N)P(O)H]_2$ (**2**) is obtained from the reaction between PCl_3 and $PhNH_2$ in toluene followed by controlled hydrolysis of the product in an H_2O–$CHCl_3$ solution. Compound **2** is the first example of P(V) dimer $[(\mu\text{-}NC_6H_5)P(H){=}O]_2$, a P_2N_2 ring with two P(O)H moieties. The reaction of **2** with $ZnCl_2$ in a molar ratio of 1 : 1 in tetrahydrofuran yields the cyclophosph(V)azane complex $Cl_2Zn[(C_6H_5N)P(O)H]_2$ (**3**) in which Zn–O bonds form directly between a cyclic phosph(V)azane ligand and Zn(II). The products have been characterized by infrared, multinuclear (^1H, ^{31}P, ^{13}C) NMR, mass spectrometry, and elemental analysis.

Keywords: Cyclic phosph(V)azane; Zinc complex; ^{31}P Spectroscopy; P_2N_2-ring

1. Introduction

Compounds containing phosphorus and nitrogen, with direct bonds between these two elements, have been employed as ligands for many years [1, 2]. Among these compounds cyclodiphosph(V)azanes as ligands have attracted considerable interest, since the four-membered P_2N_2 ring contains active positions in close proximity [3–6]. They bear active sites as hard and soft centers N, O, and P and are reactive to form various metal complexes [7–10]. The reactions of phosphazanes with molybdenum carbonyls have been extensively studied and a number of synthetic methods have been devised to form new inorganic complexes [11–13]. In addition, small heterocycles with P–N and P–O bonds have biochemical and commercial importance [7, 8].

The coordination behavior of bis(anilino)phosphine oxide [14] with Al, Si, Sn, Ti, and Pt has already been reported [15–19]. Herein we report the synthesis of the first example of P(V) dimer $[(\mu\text{-}NC_6H_5)P(H){=}O]_2$ (**2**). Some Zn(II) complexes of cyclodiphosph(V)azane have shown considerable biological and antimicrobial activities and have potential application in drug delivery systems [20]. This article will focus on the synthesis and characterization of the new ligand (**2**) and its coordination chemistry with $ZnCl_2$.

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2. Experimental

2.1. *Materials and instrumentation*

All experiments requiring inert atmosphere were carried out under nitrogen using standard Schlenk techniques. The solvents were purified and dried as indicated: Tetrahydrofuran (THF) was treated with KOH and freshly distilled twice from sodium before use. Aniline was distilled from P_4O_{10}. Toluene was distilled over sodium after refluxing for 7 h. Phosphorus trichloride was used as purchased from Merck Co. The bis(anilino)phosphine oxide $(C_6H_5NH)_2P(O)H$ (**1**) was prepared by previously reported procedures [14, 19].

NMR spectra were recorded on a Bruker Avance 400 MHz at ambient temperature. ^1H (400.13 MHz) and ^{13}C NMR (100.62 MHz) were recorded using $(CD_3)_2SO$ as a solvent with TMS as an external standard.

The ^{31}P spectra (161.97 MHz) were referenced to external 85% H_3PO_4. Infrared (IR) spectra were measured on a Bomen FT–IR spectrophotometer. FAB (+) mass spectra were recorded using a JEOL SX – 102A instrument. Elemental analysis (C, H, N) was performed by the microanalytical service of N.I.O.C Research Institute of Petroleum Industry. The zinc content for **3** was determined by flame atomic absorption spectrometry. The chloride content for **3** was measured by potentiometric titration (argentometry).

2.2. *Preparation of $[(C_6H_5N)P(O)H]_2$ (2)*

To pure aniline (26 mL) in dry toluene (50 mL) at 0°C, phosphorus trichloride (5 mL, 0.057 mmol) in dry toluene (10 mL) was added dropwise with stirring,. Then, the temperature was slowly raised to 25°C and after 2 h, chloroform (3 mL) and H_2O (1 mL) mixture was slowly added and refluxed at 90°C for 2 h. The $PhNH_3^+Cl^-$ was filtered off immediately from the hot solution by a sintered glass filter. The solvent was removed in vacuum from the filtrate and the resulting white solid was washed with cold toluene and THF. After drying under vacuum for 24 h pure $[(C_6H_5N)P(O)H]_2$ (**2**) was obtained, yield 80%, m.p. 155–157°C (dec). Anal. Calcd for $C_{12}H_{12}N_2P_2O_2$ (%): C, 51.81; H, 4.34; N, 10.07. Found (%): C, 51.75; H, 4.56; N, 9.94. IR (KBr): 2361(P–H), 1280(C–N), 1180(P=O), 872(P–N), 1568–1393(C=C); ^1H NMR (25°C, $(CD_3)_2SO$, ppm): 7.03–6.48(m, 10H, ph), 6.62(d, 2H, PH); ^{31}P NMR (25°C, $(CD_3)_2SO$, ppm): 18.82 (d, $^1J_{PH} = 639.7$ Hz); $^{13}C\{^1H\}$NMR (25°C, $(CD_3)_2SO$, ppm): 118.6(C_P), 122.5(C_m), 129.9(C_0), 140.0(C_i); Ms: *m/z* 278, 261, 202, 122, 94, 91, 79, 63, 61, 60.

2.3. *Synthesis of $Cl_2Zn[(C_6H_5N)P(O)H]_2$ (3)*

$ZnCl_2$ (0.048 g, 0.359 mmol) was dissolved in dry THF (8 mL) and added dropwise to $[(C_6H_5N)P(O)H]_2$ (**2**) (0.1 g, 0.359 mmol) in dry THF (25 mL) under N_2 at 25°C in the absence of light. The mixture was stirred for 24 h, filtered, and the solvent removed under vacuum. The resulting pale-yellow precipitate was washed with THF and dried under vacuum for 24 h to obtain pure $Cl_2Zn[(C_6H_5N)P(O)H]_2$ (**3**), yield 64%, m.p. 110–112°C (dec). Anal. Calcd for $C_{12}H_{12}N_2P_2O_2Cl_2Zn$ (%): C, 34.77; H, 2.89; N, 6.75; Cl, 17.11; Zn 15.78. Found (%): C, 34.64; H, 2.78; N, 6.68; Cl, 17.21; Zn, 15.72.

IR(KBr): 2376(P–H), 1259(C–N), 1151(P=O), 867(P–N), 1583 and 1496(C=C), 553(Zn–O). ^{1}H NMR (25°C, $(CD_3)_2SO$, ppm): 6.63–7.11(m, 10H, ph), 6.71(d, 2H, PH); ^{31}P NMR (25°C, $(CD_3)_2SO$, ppm): 19.02(d, $^1J_{PH} = 641.3$ Hz); $^{13}C\{^1H\}$NMR (25°C, $(CD_3)_2SO$, ppm): 116.0 (C_P), 118.3(C_m), 129.4(C_0), 146.0(C_i).

3. Results and discussion

The principal starting material for these investigations, $(C_6H_5NH)_2P(O)H$ (**1**) is prepared in good yield by the reaction between of PCl_3 with $PhNH_2$ in a molar ratio of 1 : 5 through reaction (1).

$$PCl_3 + 5PhNH_2 + H_2O \rightarrow (C_6H_5NH)_2P(O)H + 3C_6H_5NH_3Cl. \qquad (1)$$

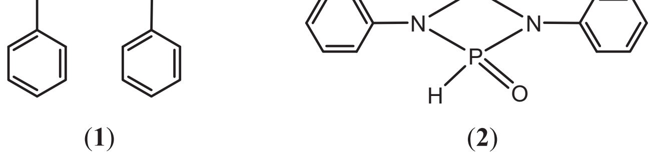
Compound **2** is produced in a condensation reaction of **1** by elimination of two aniline molecules as shown in reaction (2) (scheme 1).

$$2[(C_6H_5NH)_2P(O)H] \xrightarrow{90^\circ C} [(C_6H_5N)P(O)H]_2 + 2PhNH_2. \qquad (2)$$

Compound **2** is a very stable solid with a P_2N_2 ring, which is the first example of P(V) dimer $[(\mu\text{-}NC_6H_5)P(H){=}O]_2$, and it has the potential to act as a precursor for obtaining new phosphorus–nitrogen macrocycles and complexes. A compound of composition $[(\mu\text{-}NC_6H_5)P(H){=}O]_2$ has been mentioned by Wright *et al.* [21] as a minor contaminant in a reaction, however, its isolation and characterization was not accomplished. It should be noted that **2** is also the first P_2N_2 ring with two P(O)H moieties instead of one P(O)H moiety reported by Kumara Swamy *et al.* [22]. Compound **2** was reacted with $ZnCl_2$ in 1 : 1 molar ratio in dry THF at 25°C and the new complex $Cl_2Zn[(C_6H_5N)P(O)H]_2$ (**3**) is obtained as pale-yellow powder in 64% yield through reaction (3) (scheme 2).

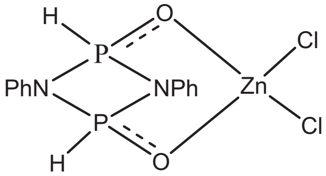
$$ZnCl_2 + [(C_6H_5N)P(O)H]_2 \rightarrow Cl_2Zn[(C_6H_5N)P(O)H]_2. \qquad (3)$$

The coordination occurs through oxygens of the ligand. Similar situation is seen in the reaction of **1** with organotin halides [17, 19]. All manipulations were carried out in an inert atmosphere. The new products, **2** and **3**, were characterized by IR, mass, and (^{1}H, ^{31}P, ^{13}C) NMR spectroscopy as well as elemental analysis. All attempts to grow single crystals of these new compounds suitable for X-ray crystallography were unsuccessful.



(**1**) (**2**)

Scheme 1. The formula of bis(aniline)phosphine oxide (**1**) and new cyclic phosphazane ligand (**2**).



(3)

Scheme 2. The formula of cyclophosph(V)azane zinc complex.

3.1. *IR spectra*

IR spectra indicate that **2** shows strong bands at 2361, 1259, 1185, and in the region of 1568–1393 cm^{-1}, assigned to P–H, C–N, P=O, and C=C vibrations, respectively. The IR spectrum also showed the absence of N–H bands of ligand which usually appear at 3334 cm^{-1}. IR spectrum for **3** shows that the P=O stretching shifted by almost 34 cm^{-1} to lower frequency upon coordination, as a result of decrease in the P=O bond order. The appearance of a new band at 553 cm^{-1}, assigned to Zn–O bonds [20], supports the bonding of zinc to oxygen.

3.2. *^{1}H NMR spectra*

The ^{1}H NMR spectrum of **2** exhibited phenyl-protons at δ 6.48–7.03 ppm and P–H as a doublet at δ 6.62 ppm with $^{1}J_{PH} = 640.1$ Hz. The ^{1}H NMR of **3** showed phenyl and P–H resonances with the appropriate relative intensities at δ 6.63–7.11 ppm as a multiplet and δ 6.71 ppm as a doublet.

3.3. *^{31}P NMR spectra*

The presence of P(O)H rather than the P(OH) in **2** is readily deduced from the proton-coupled ^{31}P NMR spectrum [14]. One signal occurs as a doublet at δ 18.82 ppm with $^{1}J_{PH} = 639.7$ Hz in the ^{31}P NMR spectrum of **2**, which is in the region associated with P(V) oxide species. The relatively large $^{1}J_{PH}$ coupling constant (639.7 Hz) is also consistent with that of a directly bonded hydrogen. In the ^{31}P NMR spectrum of **3** only one signal is seen at δ 19.52 ppm with $^{1}J_{PH} = 641.3$ Hz.

3.4. *^{13}C NMR spectra*

The $^{13}C\{^{1}H\}$NMR of **2** showed characteristic bands at 118.6(C_P), 122.5(C_m), 129.9(C_0), and 140.0(C_i) ppm. Also, $^{13}C\{^{1}H\}$NMR spectrum of **3** exhibited four characteristic signals in the aromatic region at 116.0(C_P), 118.3(C_m), 129.4(C_0), and 146.0(C_i) ppm.

3.5. *The mass spectra data*

The mass spectrum of **2** showed a strong parent peak at *m*/*z* 278 attributable to the molecular ion, along with a series of less intense peaks at *m*/*z* 60 [N–PH–N], 61 [N–P=O], 63 [NH–P–OH], 79 [HPNHPH], 91 [C_6H_5–N], 94 [$H_2P_2N_2H_2$], 122 [OP_2N_2O], 202 [M^+–C_6H_5], 261 [M^+–OH], and 278 [$M^{\cdot+}$]. The mass spectrum of **3** exhibited a low intensity peak at *m*/*z* 414 assigned to the molecular ion of $C_{12}H_{12}N_2P_2O_2Cl_2Zn$ and a relatively intense mass line at *m*/*z* 278 [$(C_6H_5N)P(O)H]_2$. Characteristic mass envelopes of phenylamido-containing phosphorus species in a similar manner to **2** are also seen for **3**, consistent with the presence of **2** in the complex.

4. Conclusions

This article has described the synthesis and spectral characterization of the first example of a P_2N_2 ring with two P(O)H moieties, [(μ-NC_6H_5)P(H)=O$]_2$. The product was obtained cleanly and used as a ligand to react with zinc dichloride to afford the desired phosph(V)azane complex. The new ligand and its zinc complex have been fully characterized by IR, multinuclear (^{1}H, ^{31}P, ^{13}C) NMR, mass spectrometry, and elemental analysis.

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