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LETTERS TO THE EDITOR

Synthesis and Structure of *N*-Thiophosphorylthiourea Containing 2,6-Diaminopyridine Fragment

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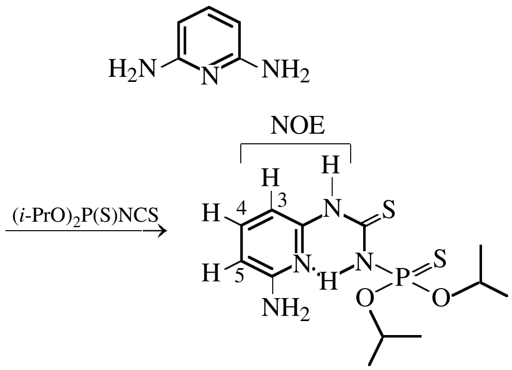
α-Aminopyridines [1] and *N*-acylamidophosphates [2, 3] are widely used as the ligands with the 1,3-*N,N*- and 1,5-*S,S*-coordination respectively. They effectively bound d-metal cations. It seemed promising to introduce both these fragments on one molecule to form a ligand capable of binding *d*-metal cations by two different ways.

With this purpose we carried out the addition of 2,6-diaminopyridine to *O,O*-diisopropylthiophosphoric acid isothiocyanate. The reaction was carried out in 2 : 1 molar reagent ratio, but the product obtained was of 1 : 1 composition. The thiourea **I** was isolated in high yield (98%). It is the fine crystalline grey powder, mp 190.3195°C with decomposition, ^{31}P NMR spectrum (acetone-d_6), δ_P 59.07 ppm. Boiling of the thiourea **I** with the isothiocyanate excess in acetone also gave no product of 1 : 2 composition.



I

The composition of the product **I** was confirmed by the elemental analysis and MALDI-TOF spectrometry using *p*-nitroaniline matrix. The MALDI spectrum of the compound obtained contains an intense peak of the molecular ion (*m/z*) 350 $[M + H]^+$.

Presence of the NH group in the molecule of thiourea **I** was confirmed by three absorption bands at 3200, 3400, and 3450 cm^{-1} in the IR spectrum. The ^{1}H NMR spectrum besides the signals of the isopropyl group protons contains a broadened signal of the NH_2 group at 5.5 ppm. The ratio of integral intensities of the isopropyl group and the pyridine protons unambiguously confirms the composition of the product. The protons of NHC(S)NHP(S) fragment are revealed in the ^{1}H NMR spectrum as the broadened signals of equal intensity at δ 9.78 ppm and 13.58 ppm. According to the published data [2] the signal of the RNH group proton in the phosphorylated thioureas of the general formula $RNHC(S)NHP(S)O'_2$ is always located downfield as compared to the NHP proton signal. But presence of the NOE cross peaks between the signal at δ 9.78 ppm and the signal of the C^3H proton of the pyridine fragment in the ^{1}H 2D NOESY spectrum unambiguously permits to attribute the upfield signal to the PyNH proton, and the downfield one to the NHP fragment.

We propose that the unusually high chemical shift value of the NHP group proton is caused by its participation in the formation of the intramolecular hydrogen bond.

***N*-(6-Aminopyridin-2-yl)-*N*'-diisopropylphosphorylthiourea.** Yield 98%, mp 190–195°C (with decomposition). IR spectrum (vaseline oil), ν, cm^{-1}: 3200, 3400, 3450 (NH); 1532 (br.s) (S–C–N); 996 (br.v.s) (P–O–C); 608 (br.m) (P=S). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.36 d (6H, CH_3, $^3J_{HH}$ 6.2 Hz), 1.37 d (6H, CH_3, $^3J_{HH}$ 6.2 Hz), 4.92 d.sept (2H, OCH, $^3J_{POCH}$ 10.7 Hz, $^3J_{HH}$ 6.2 Hz), 5.54 s (2H, NH_2), 6.33 s (1H, C^5H, $^3J_{H^5H^4}$ 8.2 Hz), 6.41 d (1H, C^3H, $^3J_{H^3H^4}$ 7.7 Hz), 7.48 br.t (1H, C^4H, $^3J_{H^3H^4} \approx {}^3J_{H^4H^5}$ 8.0 Hz), 9.78 s (1H, PyNH), 13.58 d [1H, P(S)NH, $^2J_{PNH}$ 10.9 Hz]. $^{31}P\{^1H\}$ NMR spectrum (acetone-d_6): δ_P 59.07 ppm. $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$): δ_P 57.24 ppm.

The IR spectra were recorded on a Specord M-80 spectrometer in the range 400–3600 cm^{-1} for the suspensions in vaseline oil. The ^{1}H NMR spectra were taken on a Varian Unity 300 (300 MHz) spectrometer in acetone-d_6 against internal HMDS. The ^{31}P NMR spectra were obtained on a Varian Unity 300 (121.42 MHz) spectrometer against external 85% phosphoric acid. The matrix-activated laser desorption/ionization (MALDI) mass spectra were obtained on a flight time Thermo Bioanalysis Finnigan Dynamo MALDITOF mass spectrometer. Laser desorption was carried out by means of the impulse UV laser (337 nm). Nitroaniline was used as a matrix. The samples were obtained by means of the dried drop procedure. A mixture of the acetone matrix solution (1% mass)and the acetone solution of the compound under study (0.1% mass) was placed on an underlying material and dried at 40°C.

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