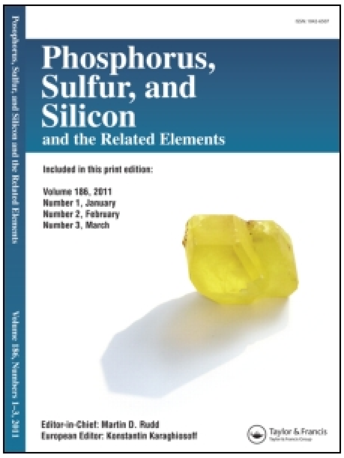

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Synthesis and Preliminary Complexation Studies of Dialkylphosphorylthiourea and Guanidines

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SYNTHESIS AND PRELIMINARY COMPLEXATION STUDIES OF DIALKYLPHOSPHORYLTHIOUREA AND GUANIDINES

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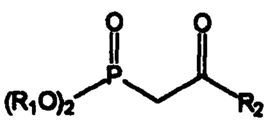
Organic compounds containing a 1-phosphoryl-2-aza-3-thiocarbonyl group (**IIa**) or a 1-phosphoryl-3-imino group (**IIb–g**) were prepared by a two phases reaction between dialkylphosphite and thiourea or the appropriate guanidine. The complexation studies carried out by UV titration method and conductivity measurements showed that these ligands complex metal ions like Cu^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+} and Al^{3+} in neutral solution.

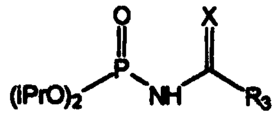
Key words: Dialkylphosphoryl compounds, diisopropylphosphoryl thiourea, diisopropylphosphoryl guanidine, complexation studies, conductivity studies.

INTRODUCTION

Bidentate compounds containing a 1-phosphoryl-3-carbonyl group (I) are known to form colorful complexes with various metal ions.[1] They are powerful extractants for trivalent lanthanides and actinides as well as alkali metal cations.[2,3] An alter-

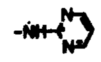
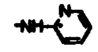


(I)



(II)

	X	R_3
a.	S	NH_2
b.	NH	SCH_2CH_3
c.	NH	NH_2
d.	NH	$N(CH_2CH_3)_2$
e.	NH	NHC_6H_{11}

	-NH-(C=X)-R3
f.	
g.	

nation of the molecular structure might improve the extractant properties of these compounds, such as complexing capacity and selectivity. Due to this background some new organic phosphorous compounds containing 1-phosphoryl-2-aza-3-thiocarbonyl or -3-imino groups (**IIa–IIe**) were prepared.

(IIb) **(IId) or (IIe)**

The thiourea and alkyl isothiourea were easily phosphorylated in a mixture of sodium hydroxide/water and diisopropyl phosphite in carbon tetrachloride solution. Guanidine was phosphorylated in the same way in good yield. The novel chemical property of the phosphorylated S-ethylisothiourea (**IIb**) is the amino group replacement for the ethylthio group in it.[4]

EXPERIMENTAL

The NMR spectra (^{1}H, ^{13}C and ^{31}P) were recorded on a Bruker AC-300 or AM-500 spectrometer. All chemical shifts are reported with respect to TMS or H_3PO_4. IR spectra were obtained on a Perkin-Elmer model 1710 spectrometer. The UV and visible spectra were taken on a Varian DMS-80 spectrophotometer. The conductivity studies were carried out on a conductometer Digimid CD-20. Melting points were taken on a Fisher-Johns melting point apparatus without correction.

Preparation of Diisopropylphosphoryl-Thiourea and -Guanidine. General Procedure: Thiourea or guanidine (0.01 mole) and sodium hydroxide (0.02 mole) were dissolved in a mixture of 5 ml of water and 2 ml of ethanol. This solution was cooled to 0°C and a solution of diisopropylphosphite (0.01 mole) in 5 ml of carbon tetrachloride was added dropwise. The mixture was then warmed up to room temperature and kept stirring at this temperature for 4 hours. After the reaction, 10 ml of water and chloroform (1:1) were added. The organic layer was separated and the aqueous solution was extracted three times with 5 ml of chloroform each. The organic layers were combined, washed once with 3 ml of water and dried over anhydrous magnesium sulphate. Then the solvent was removed in vacuum to give a crude product.

Diisopropylphosphorylthiourea (**IIa**)[4], diisopropylphosphoryl-S-ethylisothiourea (**IIb**)[4] and diisopropylguanidine (**IIc**)[4] were prepared in good yield by following the general procedure.

N,N-diethyl-N'-diisopropylphosphorylguanidine (**IId**): Diisopropylphosphoryl-S-ethylisothiourea (**IIb**) (0.001 mole, 0.26 g) and diethylamine (0.01 mole, 0.73 g) were dissolved in 5 ml of toluene. The solution was refluxed for 24 hours. After the reaction the excess diethylamine and solvent were removed to give a semi-solid. This crude product was purified by column chromatography using chloroform as solvent, the isolated product was then recrystallized from petroleum ether to give 0.24 g (82%) of pure product, m.p. 55–57°C. IR (KBr plate) cm^{-1}: 3429, 3321 (NH), 1595 (C=N), 1562, 1198 (P=O), 994 (P—O). NMR-^{1}H: ($CDCl_3$) δ: 1.10 (t, $J = 7.0$ Hz, 6H), 1.23 (d, $J = 6.0$ Hz, 12H), 3.30 (q, $J = 7.0$ Hz, 4H), 4.33–4.53 (m, 2H), 6.07 (2H, broad singlet); NMR-^{13}C: 13.1, 23.7 (CH_3), 41.6 (CH_2N), 69.4 (CHO), 156.5 (C=N); NMR-^{31}P: 6.54. MS (m/e): 280 ($M^+ + 1$).

N-Cyclohexyl-N'-diisopropylphosphorylguanidine (**IIe**): Compound (**IIb**) (0.002 mole, 0.54 g) and cyclohexylamine (0.004 mole, 0.40 g) were dissolved in 5 ml of toluene. This solution was refluxed for 24 hours. After the reaction the excess cyclohexylamine and the solvent were removed to give a wet solid as crude product. Recrystallization from petroleum ether gave 0.52 g (85%) of pure product, m.p. 96–98°C. IR (KBr plate) cm^{-1}: 3364, 3232 (NH), 1651 (C=N), 1110 (P=O), 994 (P—O). NMR-^{1}H δ: 1.10–1.38 (m, 18H), 1.60–1.80 (m, 4H), 3.55 (broad singlet, 1H), 4.30–4.60 (m, 2H), 6.08 (broad singlet, 3H); NMR-^{13}C: 23.8 (CH_3), 24.7, 25.5, 33.0 (CH_2), 49.2 (C—NH), 69.7 (CH—O), 157.4 (C=N); NMR-^{31}P: 6.36. MS (m/e): 306 ($M^+ + 1$).

2-Diisopropylphosphorylaminopyrimidine (**IIf**): Following the general procedure, 5 ml (0.03 mole) of diisopropylphosphite reacts with 0.03 mole of 2-aminopyrimidine for 12 hours. After the reaction some starting material was separated as crystals from the reaction mixture. The crude product (oil) was purified by column chromatography using ethylacetate as solvent. White crystals were isolated; m.p. 158–159°C. IR (KBr plate) cm^{-1}: 3400 (N—H), 2990 (C—H), 1580, 1550, 1440 (C=C, C=N—), 1240 (P=O), 1020 (P—O—). NMR-^1H ($CDCl_3$) δ: 1.21, 1.33 (d, J = 6.1 Hz, 12H), 4.65–4.75 (m, 2H), 6.80 (t, J = 4.7 Hz, 1H), 8.54 (d, J = 6.9 Hz, 1H) and 8.99 (d, J = 9.7 Hz, 1H); NMR-^{13}C: 23.5, 23.9 (CH_3), 71.1, 77.0 (—C—H), 114.1, 158.4 and 159.5 (aromatic carbons); NMR-^{31}P: −4.4. MS (m/e): 259 (M^+).

2-Diisopropylphosphorylaminopyridine (**IIg**): Following the general procedure, 0.03 mole each of diisopropylphosphite and 2-aminopyridine were used. Triethylamine was used instead of sodium hydroxide. Yellow crystals (m.p. 123–128°C) were obtained. Recrystallization from a hexane/chloroform mixture (1:1) gave 8.3 g (40, 20% yield) of white crystals, m.p. 128–129°C. IR (KBr plate) cm^{-1}: 3087, 2900 (—NH, C=C—H, C—H), 1600, 1582, 1499, 1437 (C=C aromatic, C=N—), 1387, 1377 (C—H), 1238 (P=O), 1000 (P—O—). NMR-^1H ($CDCl_3$) δ: 1.21, 1.35 (d, J = 6.1 Hz, 12H), 4.55–4.75 (m, 2H), 6.85–7.11 (m, 2H), 7.45–7.60 (m, 1H), 8.33 (broad singlet, 1H) and 8.53 (d, J = 4.2 Hz, 1H); NMR-^{13}C: 23.6, 23.8 (CH_3), 71.8, 71.9 (C—H), 108.2, 110.8, 116.8, 137.9 (aromatic carbons); NMR-^{31}P: −3.0. MS (m/e): 258 (M^+).

Complexation Studies

By UV spectroscopy: Inorganic salts were used as purchased and kept under nitrogen in a desiccator. The "ligand solutions" in anhydrous methanol were prepared by diluting a 0.1 M stock solution to the expected suitable concentration. For the differential spectra, an inorganic salt solution was placed in the reference cuvette. Metal ion solutions were prepared in 0.01 M, 0.1 M and 1.0 M concentrations; these solutions were added to the ligand solution through a 10 μl GC syringe so that the volume changes could be neglected. After each addition, the cuvette was thoroughly shaken before the UV spectrum was recorded. For the qualitative studies a 10 fold excess of the salts was used.

By conductance measurement: Experiments were carried out in a cell provided with platinum electrodes at 25°C. Methanol, chloroform and water were used as solvents. All solvents were triply distilled before use. The stoichiometry of the [metal ion]/[ligand] was determined by the quantity of the ligand added to a solution of metal ion concentration of 10^{-4} M. The equivalent conductivity was measured on each addition of the ligand solution. The concentrated ligand solution was added by using a 10 μl gas chromatography syringe so that the volume change of the whole solution could be neglected. A plot of equivalent conductance *vs* the ratio of [metal ion]/[ligand] gave the information of the complexation. Inorganic salts like copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$), iron (**II**) sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$), nickel (**II**) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), aluminum sulphate octadecahydrate [($Al_2(SO_4)_3 \cdot 18H_2O$)] lead (**II**) acetate trihydrate [($(CH_3CO_2)_2Pb \cdot 3H_2O$)], cobalt (**II**) acetate tetrahydrate [($(CH_3CO_2)_2Co \cdot 4H_2O$)], cadmium acetate dihydrate [($(CH_3CO_2)_2Cd \cdot 2H_2O$)], zinc acetate dihydrate [($(CH_3CO_2)_2Zn \cdot 2H_2O$)] and mercury (II) chloride ($HgCl_2$) were used.

RESULTS AND DISCUSSION

Diisopropylphosphorylthiourea (**IIa**) presents UV absorption peaks at 202 nm and 254 nm. Compounds containing a 1-phosphoryl-2-aza-3-imino group (**IIc–IIg**) present strong absorption peaks around 210 nm and a much weaker peak around 250 nm. When a solution of the metal ion is added the spectrum shows an increase or decrease in its absorption intensity and/or new peaks if a metal complex is formed. No change in the spectrum is observed if there is no complex formation. Figure 1 shows the changes in the UV spectra before and after the ten fold addition of the metal ion to the solution of diisopropylphosphorylthiourea (**IIa**). In the complexation reaction with Cu^{2+} (Figure 1b) there is a significant change in the absorption intensity: the absorption wavelength is shifted from 254 nm to 240 nm and a new peak appears at 348 nm. Compound **IIa** shows complexing properties towards Cu^{2+},

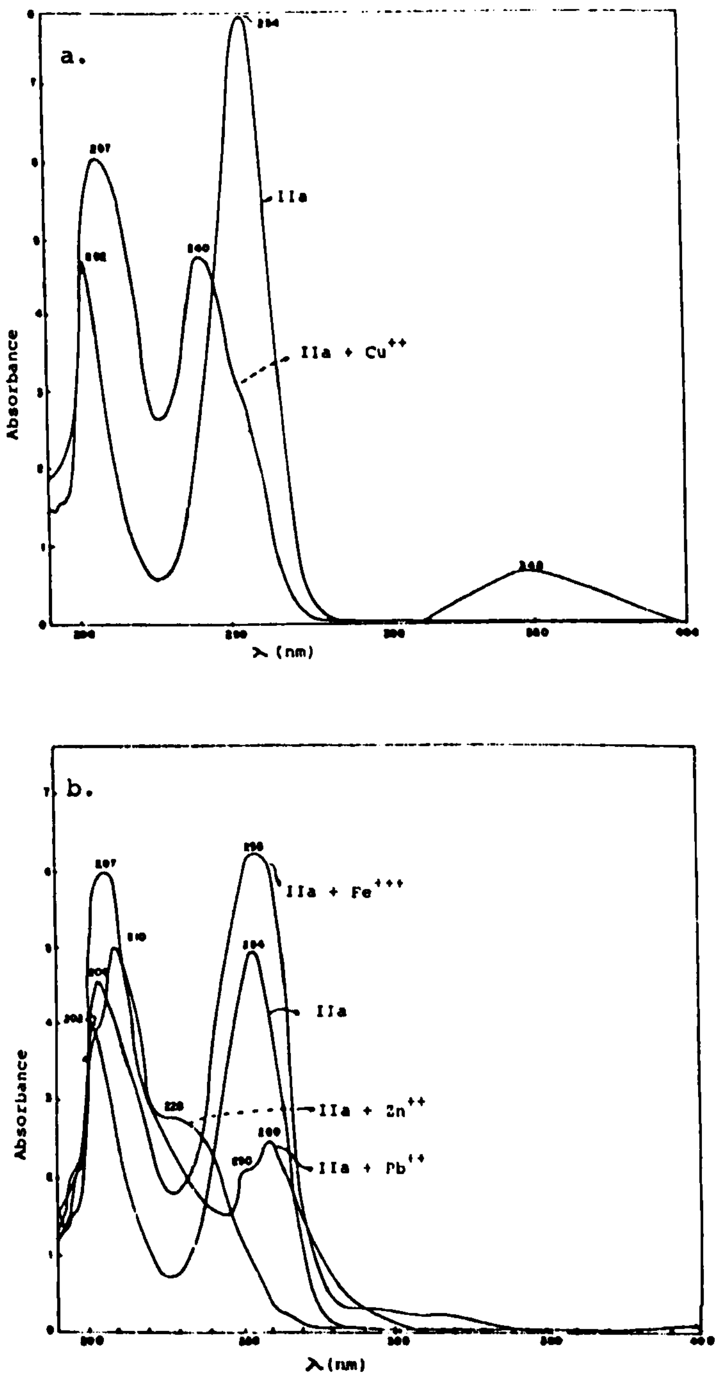


FIGURE 1 Ultraviolet spectra of diisopropylphosphorylthiourea (**IIa**) and its complexes in methanol ($[M^{+n}]/[L] = 10$) a. [**IIa**] $= 6.5 \times 10^{-5}$ M, b. [**IIa**] $= 5 \times 10^{-5}$ M.

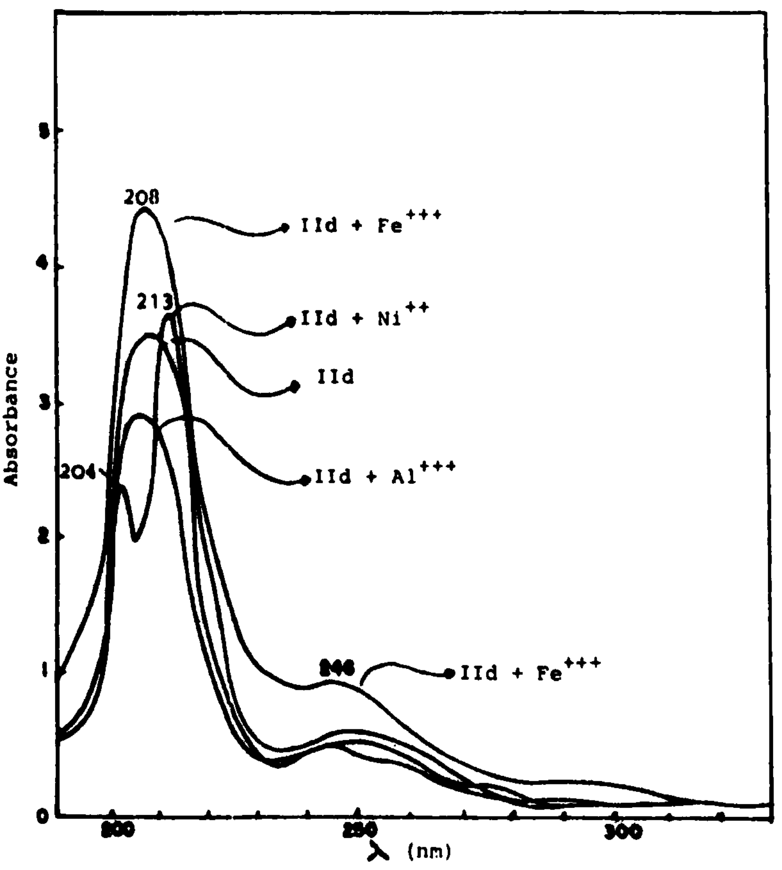


FIGURE 2 Ultraviolet spectra of N,N-diethyl-N′-diisopropyl phosphorylguanidine (**IId**) and its complexes in methanol ($[M^{+n}]/[L] = 10$), [**IId**] = 1.01×10^{-4} M.

Zn^{2+}, Pb^{2+}, Fe^{3+}, Ni^{2+} and Al^{3+} in neutral solution. Diisopropylphosphorylguanidine **IIc** complexes Pb^{2+}, Fe^{3+}, Ni^{2+} and Al^{3+}. Very little changes in the UV spectra are observed when solutions of Cu^{2+} and Zn^{2+} are added to the ligand solution. This behaviour changes when alkyl groups are introduced into the system (Figure 2). The alkylated phosphorylguanidines **IId** and **IIe** can complex all metal ions mentioned above.

The existence and stoichiometry of the complexes can also be demonstrated by electric conductance measurements. Equivalent conductance of the metal ion solution is measured in the presence of different ratios of an appropriate ligand within 3% accuracy. Systems containing the 1-phosphoryl-2-aza-3-thiocarbonyl group (**IIa**) or the 1-phosphoryl-2-aza-3-imino group (**IIc–IIe**) can complex Cu^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}, Zn^{2+}, Pb^{2+}, Fe^{3+}, Ni^{2+}, Ca^{2+} and Al^{3+}; compounds **IIf** and **IIg** complex Al^{3+} and Hg^{2+} by this method. Figure 3 shows plots of some titration curves.

The addition of ligand **IIa** to a 10^{-4} M solution of Hg^{2+} leads to the formation of a 2:1 complex. The increase in the conductance during the titration suggests that the mercury salt initially is undissociated in methanol. With the addition of

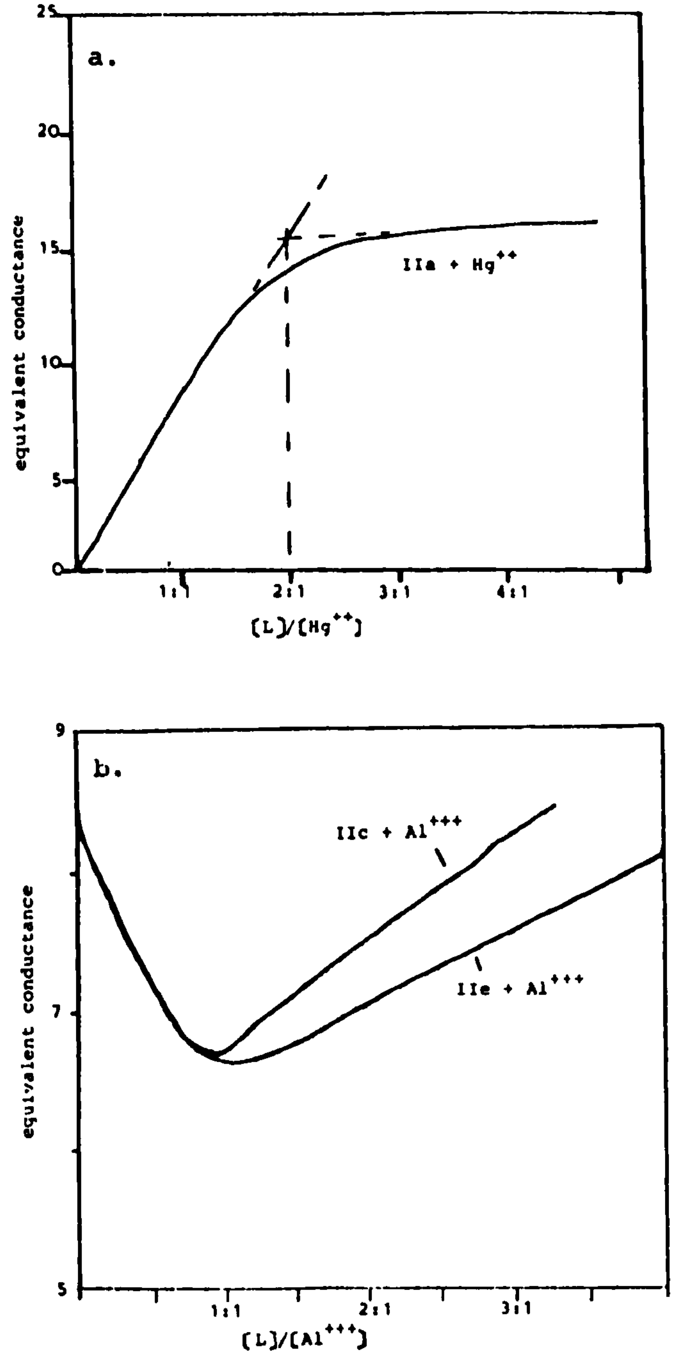
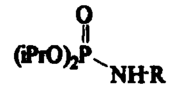


FIGURE 3 Equivalent conductance of $HgCl_2$ and $Al_2(SO_4)_3$ in methanol at 25°C in the presence of compounds a. **IIa**; b. **IIc** and **IIe**. $[M^{+n}] = 1 \times 10^{-4}$ M.

the ligand, the mercury ion is complexed by the organic ligands and thus increases the dissociation of the ion pairs, which results in an appreciable conductance increase. In the titration studies of Al^{3+} with the ligands **IIc** and **IIe** (Figure 3b), the aluminum sulphate is highly dissociated at the beginning; with the addition of **IIc** or **IIe**, the formation of the complex increases the concentration of the ion pairs, thus decreases the mobility of the ions and in consequence decreases the conductivity of the solution. After the titration curve reaches a minimum (the formation of a 1:1 complex) the presence of excess ligand would increase the organic surrounding of the metal ion and thus would increase the ions separation of the ion pair formed initially. This would, in consequence, increase the conductivity. No definite complex is further observed.

Compound **IIa** forms a 3:1 complex with Cu^{2+}, a 1:1 complex with Al^{3+} and a 2:1 complex with Hg^{2+}; compound **IIc** forms a 1:2 complex with Cu^{2+}, a 1:1 complex with Al^{3+} and a 2:1 complex with Hg^{2+}; compound **IIe** forms a 1:1 complex with Al^{3+}. No definite complex formation beyond the change in conductivity is observed from the rest of the titration studies on different ligands. Simple diisopropylphosphoramidates (**III**) show no significant complexation toward the metal ions studied under the same conditions.

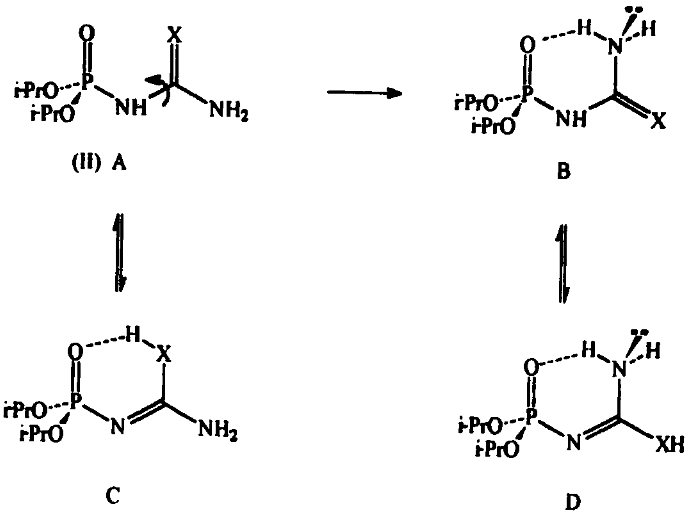


$(iPrO)_2P(=O)NH{-}R$

(IIIa) $R{=}C_6H_5$

(IIIb) $R{=}C_3H_7$

It is known that the 1,3-dicarbonyl compounds enolize easily one of its carbonyl groups to give a six membered structure with an intramolecular hydrogen bonding bridge. Compounds containing a 1-phosphoryl-2-aza-3-carbonyl group can also be presented in a similar way in many forms.



X-ray diffraction structural analysis of **IIc**[5] reveals that structures C and D predominate in the solid state. The coordination of the P atom in the molecule is distorted tetrahedrally, O(3)—P—O(2) and O(2)—P—N(1) angles are increased

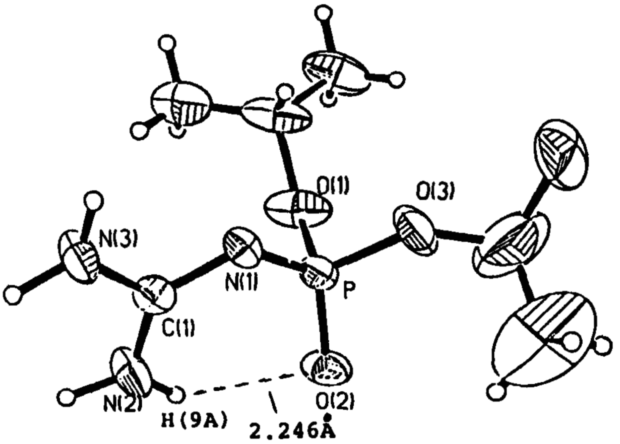
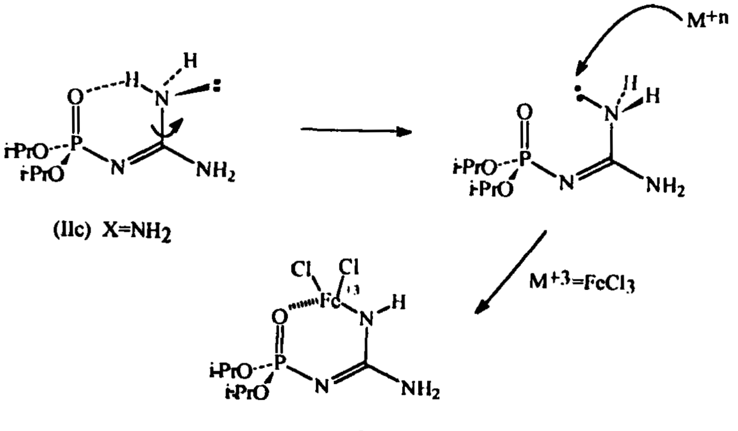


FIGURE 4 Molecular structure of compound IIc.

and O(3)—P—O(1), O(2)—P—O(1) and O(3)—P—N(1) angles are decreased from the ideal value 109.5° while O(1)—P—N(1) is maintained at its ideal value. The P—N bond length is in the range of the corresponding amidophosphate (1.61–1.71 A°).[6] The bond lengths of P=O(2), P—O(1) and P—O(3) are normal. The bond length of C(1)—N(1) is 1.351(5) A°, C(1)—N(3) is 1.364(9) A°. Both are shorter than a normal C—N single bond (1.47 A°) and greater than a simple C=N bond (1.30 A°). The bond length of C(1)—N(2), 1.330(9) A°, indicates double bond character. Sum of the bond angles around C(1) is 360.0°. These data suggest planarity around C(1) atom and strong resonance between carbon and nitrogen. No hydrogen atom connected to N(1) is observed. The calculated distance between H(9A) . . . .O(2) is 2.246 A°, this suggests hydrogen bonding of P—O(2) . . . H—N(2) in the crystal structure.

When a metal cation is introduced to the ligand solution the intramolecular



(IIc) X=NH2

(IIc-Fe+3)

hydrogen bridge can be easily cleaved by a simple rotation of the C—N bond and thus creates a coordination site for the complexation of metal cation.

A complex of **IIc** and Fe^{3+} is prepared and identified as a 1:1 chelate[5]:

ACKNOWLEDGEMENTS

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5. a) Marcos C. de Souza, Ph.D thesis, Instituto Militar de Engenharia (1994); b) Selected bond lengths (A°): P—O(1) 1.585(5); P—O(2) 1.460(5); P—O(3) 1.597(7); P—N(1) 1.610(5); N(1)—C(1) 1.351(9); C(1)—N(2) 1.330(9); C(1)—N(3) 1.364(9). Selected angles (°): N(1)—C(1)—N(2) 125.9(6); N(1)—C(1)—N(3) 117.5(6); N(2)—C(1)—N(3) 116.6(6); O(2)—P—O(1) 107.1(3); O(3)—P—O(1) 105.2(4); O(3)—P—O(2) 114.0(3); N(1)—P—O(1) 109.5(3); N(1)—P—O(2) 119.8(3); N(1)—P—O(3) 100.3(3).
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