Journal of Molecular Structure 1036 (2013) 35–41

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis, crystal structure and spectral properties of diammonium dihydrogen N-(methylene-2-pyridine)-N,N,-di-(methylenephosphonate)

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HIGHLIGHTS

- Synthesis, X-ray structural and spectroscopic characterization of N-(methylene-2-pyridine)-N,N,-di(methylenephosphonic) acid are presented.
- Lowest dissociation constants (unavailable with other methods) were determined.

ARTICLE INFO

Article history:
Received 19 March 2012
Received in revised form 3 September 2012
Accepted 19 September 2012
Available online 2 October 2012

Keywords:
Aminophosphonic acid
Heterocyclic compound
X-ray crystal structure
NMR spectroscopy
Acid-base equilibria

ABSTRACT

In this paper synthesis, crystal structure and spectral properties of a new, N-(methylene-2-pyridine)-N,N,-di-(methylenephosphonic) acid (hereinafter **IV**) are reported. The X-ray structure analysis revealed that in crystal of the ammonium dihydrogen N-(methylene-2-pyridine)-N,N-di(methylenephosphonate) (hereinafter **V**) two of the six oxygen atoms from phosphonic groups are protonated and form strong hydrogen bonds, moreover the N(pyridine) and N(amino) atoms are deprotonated. The acid–base properties of studied compound in aqueous solution indicated that the dissociation constants pK_{1dis} 0.70 ± 0.03 and pK_{2dis} 0.98 ± 0.05 are very similar to that determined for nitrilotri(methylphosphonic) acid.

1. Introduction

Since the polyaminophosphonic acids were synthesized for the first time [1], interest in these compounds has continually been growing [2]. Due to high basicity of the phosphonic oxygen atoms [3], phosphonic ligands interact with metal cations more strongly than their carboxylic analogs, hence the stability constants of metal phosphonates are often several orders greater than those of carboxylates [4]. For this reason aminophosphonates are a promising group of chelate ligands for d- and f-elements [5]. Such compounds have been investigated for their biological activity [2c,2l,5b], potential applications as MRI contrast agents [6] as well as their photophysical properties [7]. However tailoring of the compound with desired properties require addition of specifically customized functional groups; for example substitution of one of the phosphonic group by an aromatic substituent predispose such a ligand to investigate its photoluminescence properties. Therefore the polyaminophosphonic acids with specific chemical activity as well as outstanding physical properties have been extensively sought. The basic research of these compounds includes multi-faceted aspects, e.g. X-ray [5,7] and NMR [6,8] structural characterization, photophysical properties (UV–Vis–NIR–IR) [5,7], thermodynamic studies [2,4], theoretical calculations [3,9] as well as more specialized investigations such as analysis of experimental electron density distribution [3,9].

Several methods of synthesis of aminophosphonic acids are known, but most of them are based on Mannich type reaction (Scheme 1) [10].

The synthesis of these compounds is relatively difficult because obtaining of the pure substance and then good quality single crystals is not straightforword; it is often connected with high solubility of their salts in aqueous solution.

Another important problem concerns the acid–base properties of aminophosphonic acids in strong acidic solutions. As it was shown previously the determination of the first dissociation constants encounters some difficulties because of strong acidity of the phosphonic groups [2,11]. On the other hand, such thermodynamic parameters are important for quantitative understanding of complexation equilibria of metal ions by these kind of ligands and, furthermore, such studies may be very useful for determining pH of the solution in which the ligand molecule starts to bind to the metal ion. This is key information determining selection of an

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http://dx.doi.org/10.1016/j.molstruc.2012.09.051

$$RNH_2 + 2H_2CO + 2H_3PO_3 \xrightarrow{\Delta T} RN(CH_2PO_3H_2)_2 + 2H_2O$$

Scheme 1. Aminoalkylphosphonic acids synthesis – Mannich–type reaction.

appropriate coordination model for studies of stability constants. By using the ^{31}P NMR spectroscopy some authors managed to determine the lowest dissociation constants of the nitrilotri (methylphosphonic) acid (H_6NTP) [11], which demonstrates high affinity toward transition metal cations and has been widely used as scale inhibitors in industry [12]. The estimated values of pK_{1dis} = 0.5 ± 0.2 and pK_{2dis} = 1.0 ± 0.1 for H_6NTP confirm high acidity of aminophosphonates. It seems to be important to find out, whether and to what extent the substitution of methylphosphonic group by a group of another kind may affect the dissociation constants values of polyphosphonic acid?

Therefore in this work the synthesis as well as structural and spectroscopic studies of the new derivative of the H_6NTP acid, in which one of the phosphonic groups was replaced by the methylene-2-pyridine arm, are presented.

2. Results and discussion

The synthesis of the aminophosphonic acid (**IV**) (Scheme 2) was started from the reaction of 2-pyridinecarboxaldehyde (**I**) with hydroxylamine hydrochloride. Next the prepared oxime was converted into 2-(aminomethyl)pyridine (**III**) by the reduction with hydrogen *in statu nascendi* in acetic acid (80%). Treatment of (**III**) with formaldehyde and phosphonic acid (H_3PO_3) in solution of hydrochloric acid gave N-(methylene-2-pyridine)-N,N-di (methylenephosphonic) acid (**IV**). Next to a metanolic solution of N-(methylene-2-pyridine)-N,N-di(methylenephosphonic) acid aqueous solution of $NH_{3(aq)}$ was added and crystals of the ammonium salt (**V**) were obtained.

2.1. Crystal structure

The compound with the formula $(NH_4)_2pyCH_2N(CH_2PO_3H_2)_2$ (**V**) crystallizes in the monoclinic $P2_1/c$ space group. The crystals of the salt consist of ammonium cations and doubly protonated phosphonic anions H_2L (Fig. 1). The selected bond lengths and angles are compared in the Table 1.

The elongation of P1–O3 and P2–O5 bonds (~0.07 Å) in comparison with the remaining P–O bonds indicates that the respective oxygen atoms are protonated. The charges of both $-CPO_2(OH)^-$ are compensated by two ammonium cations. The valence angles of $-CPO_3^{2-}$ groups change between 101.93(6)° and 116.49(7)°. In the studied crystal one may distinguish layers composed of pyridyl rings interleaved with ones formed by phosphonic groups as well as NH_4^+ cations. The layers are parallel to the (0 1 0) plane (Fig. 2).

The crystal packing is determined mainly by the hydrogen bonds O–H···O and N–H···O (Table 2). The strongest D–H···A interaction is observed between phosphonic oxygen atoms O5 and O1 from a neighboring molecule (2.580(2) Å).

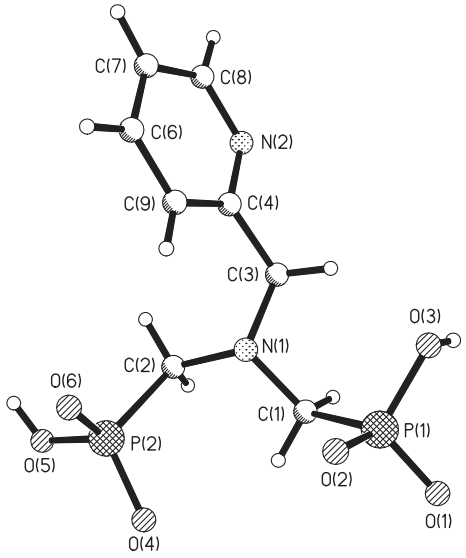
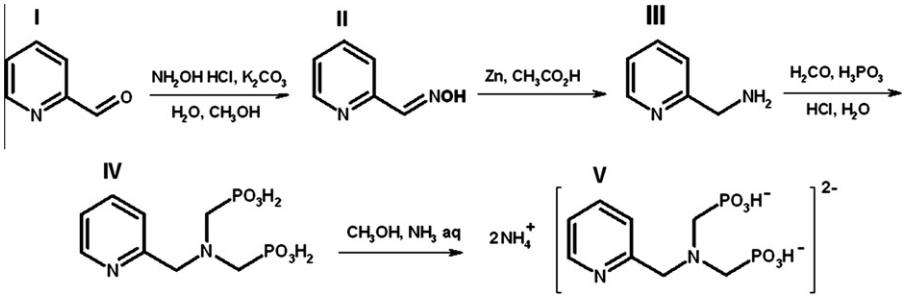


Fig. 1. Molecular structure of $[H_2NP_2py]^{2-}$ anion together with atom labels.

Table 1
Selected bond lengths (Å) and angles (°) in $(NH_4)_2H_2NP_2py$ salt.

Bond	Distance (Å)	Angle (°)	
P1–O1	1.5050(11)	O2–P1–O1	116.49(7)
P1–O2	1.4958(11)	O2–P1–O3	107.99(7)
P1–O3	1.5774(12)	O1–P1–O3	109.25(7)
P2–O4	1.4988(11)	O2–P1–C1	109.09(7)
P2–O5	1.5740(11)	O1–P1–C1	106.55(6)
P2–O6	1.5085(11)	O3–P1–C1	107.09(7)
P1–C1	1.8053(15)	O4–P2–O6	115.52(7)
P2–C2	1.8088(15)	O4–P2–O5	107.49(6)
N1–C1	1.4764(19)	O6–P2–O5	109.60(6)
N1–C2	1.4758(18)	O4–P2–C2	111.43(7)
N1–C3	1.4589(19)	O6–P2–C2	109.95(7)
N2–C8	1.342(2)	O5–P2–C2	101.93(6)
N2–C4	1.3383(19)		
C4–C9	1.386(2)		
C6–C7	1.380(2)		
C6–C9	1.382(2)		
C7–C8	1.380(2)		
C3–C4	1.501(2)		



Scheme 2. Synthesis of 2-pyridinealdoxime – (II), 2-(aminomethyl)-pyridine – (III), N-(methylene-2-pyridine)-N,N,-di-(methylenephosphonate) acid – (IV), diammonium dihydrogen N-(methylene-2-pyridine)-N,N,-di-(methylenephosphonate) – (V).

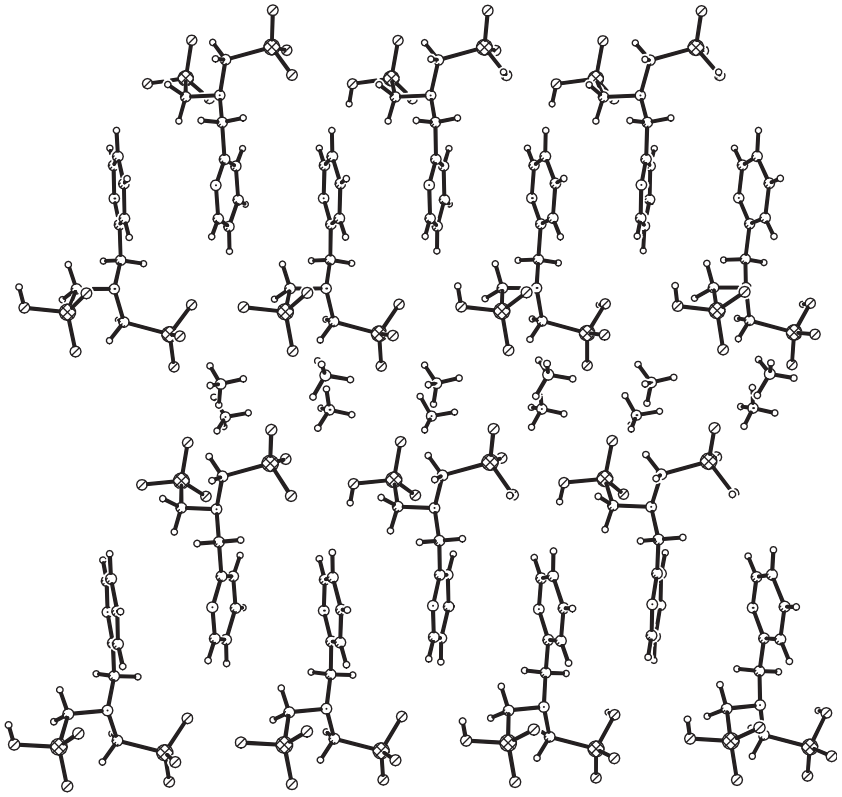


Fig. 2. The arrangement of the $[H_2NP_2py]^{2-}$ anion along the *ac* diagonal [101] direction.

Table 2
Geometry of hydrogen bonds D–H···A in $(NH_4)_2H_2NP_2py$.

D–H···A	D–H (Å)	H···A (Å)	D ··· A (Å)	D–H···A (°)
O5–H5···O1$^{(i)}$	0.82(2)	1.79(2)	2.580(2)	162
O3–H3···N2$^{(ii)}$	0.72(3)	1.98(3)	2.699(2)	177
N3–H32···O2$^{(iii)}$	0.94(2)	1.79(2)	2.713(2)	166
N4–H44···O2$^{(iv)}$	0.89(2)	1.88(2)	2.768(2)	176
N3–H31···O4$^{(v)}$	0.91(2)	2.03(2)	2.842(2)	149
N3–H34···O4$^{(vi)}$	0.87(2)	2.11(2)	2.953(2)	164
N4–H41···O1$^{(iii)}$	0.89(2)	1.95(2)	2.796(2)	158
N4–H42···O4$^{(iv)}$	0.88(2)	2.20(2)	3.022(2)	154
N4–H43···O6$^{(vii)}$	0.92(2)	1.84(2)	2.748(2)	171
N3–H33···O6$^{(iv)}$	0.85(2)	2.01(2)	2.850(2)	169

Symmetry operations: (i) x, $3/2 - y$, $1/2 + z$; (ii) $-x$, $1 - y$, $-z$; (iii) x, y, z; (iv) x, $1/2 - y$, $-1/2 + z$; (v) $1 - x$, $1/2 + y$, $1/2 + z$; (vi) x, $1 + y$, z; (vii) $1 - x$, $1 - y$, $-z$.

The analysis of the nitrogen N1 – neighbor atom distances and the overall network of the hydrogen bonds may suggest that N1 atom is deprotonated, as otherwise expected from the crystal electroneutrality condition. Interestingly in spite of that the basicity N–amino atoms are usually higher that N–pyridyl and O–phosphonic atoms [13] in studied crystals both phosphonic groups are protonated and the N2(pyridyl) atom forms hydrogen bond with an oxygen atom while the N1(amino) atom is deprotonated. If the N1(amino) atom was protonated the distance between H9 and hipotetical H(amino) would be too small (about 2 Å).

Neutronographic structure of K_2H_6EDTMP salt (where EDTMP – ethylenediaminotetra(methylenephosphonate) anion) indicates that similarly deprotonated N(amino) atoms exist in K_2H_6EDTMP crystal [14].

Because of the rotation freedom of the pyridyl group around the single C3–C4 bond the N2 atom may form the hydrogen bond with O3 from the phosphonic group belonging to an adjacent anion. For these reasons the neighboring pyridine planes are inclined 30.8° (see Figs. 2 and 3).

The hydrogen bonds together with rather weak π···π stacking (distance between the centers of the rings about 4.09 Å) give rise to a bonded network observed in the crystal structure of **V**.

2.2. NMR spectroscopy (studies in solution)

The proton spectra consist of six groups of signals with intensity ratio 1:1:1:1:2:4. The signals at 8.51, 7.92, 7.55, 7.44, 4.57 and 3.15 ppm, at pH = 6.25, correspond to positions of 6, 4, 3, 5, α and β, respectively, as it was shown in Fig. 4.

The determined coupling constants of hydrogen pyridine group are as follows: $^3J_{H6-H5}$ = 5.4 Hz $^4J_{H6-H4}$ = 1.6 Hz, $^5J_{H6-H3} \sim$ 1.5 Hz, $^3J_{H5-H4}$ = 7.7 Hz, $^4J_{H5-H3}$ = 2.2 Hz and $^3J_{H4-H3}$ = 6.4 Hz. Their values are rather typical for pyridine derivatives [15].

The resonance of methylene protons H_β splits into a doublet by coupling with phosphorus $^2J_{H\beta-P}$ = 11.2 Hz $^4J_{H\alpha-P}$ < 1 Hz at pH = 6.25. Generally the chemical shift of $H_{i=3,4,5,6}$ pyridyl protons undergoes a upfield transition (Fig. 5).

Among the observed pyridyl protone signals the H_4 and H_5 are especially sensitive to pH variation hence may corresponds to deprotonation of pyridyl nitrogen atom which occur at about pH ~ 5–6. This result is consistent with potentiometric and spectroscopic data obtained for 6-phosphonopyridine-2-carboxylic acid and -3-carboxylic acid and (pyridyl-2-ylmethyl)-phosphonic acid for which deprotonation of the pyridyl ring nitrogen occurs between pH 3 and 6 [16].

Also the coupling constants $^2J_{H\beta-P}$ is sensitive to changes of pH of solution as it was shown in Fig. 6. The largest $^2J_{H\beta-P}$ changes are observed between pH 3–6 and 10.5–14, what may be connected with deprotonation of $O(PO_3^{2-})$ and N(amino) atoms, respectively.

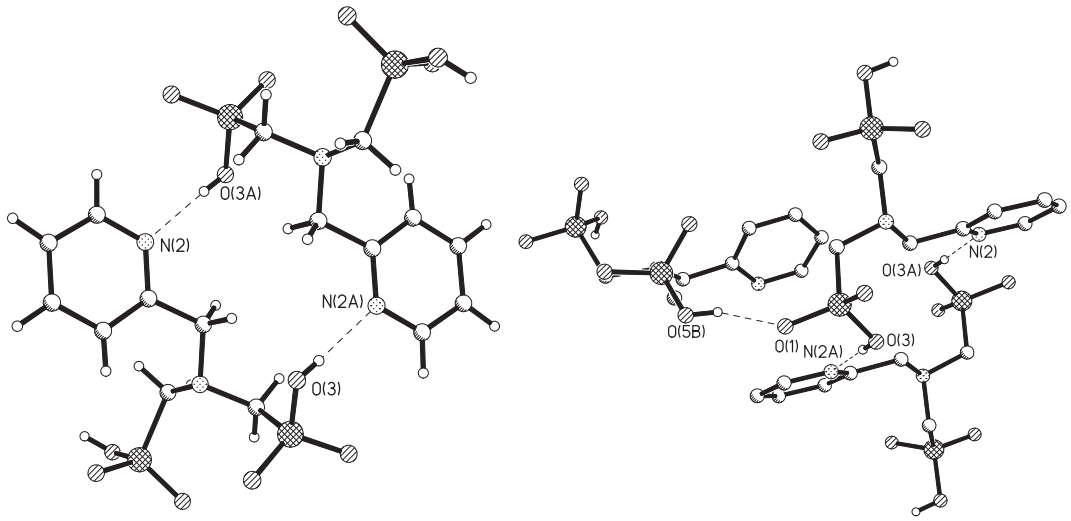


Fig. 3. The selected hydrogen bonds in $(NH_4)_2H_2NP_2py$ crystal.

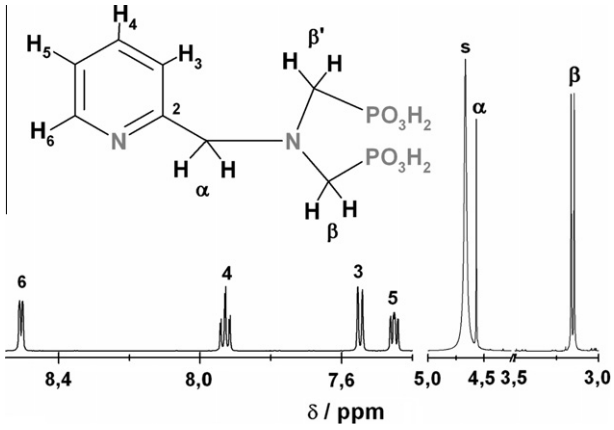


Fig. 4. ^1H NMR spectra of $(NH_4)_2H_2NP_2py$ salt in D_2O at pH 6.25.

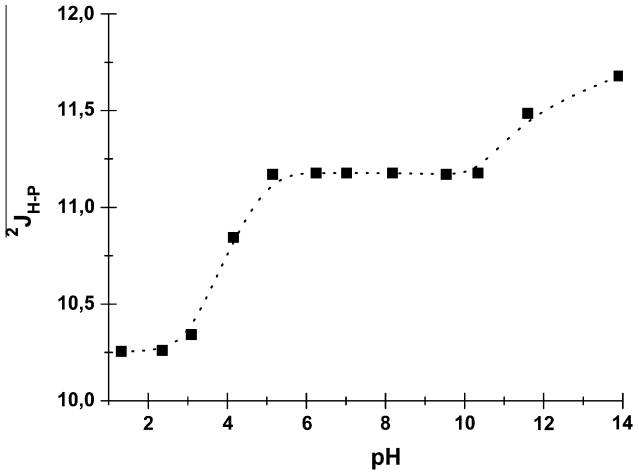


Fig. 6. pH dependence of coupling constants of methylene protons H_6 signal.

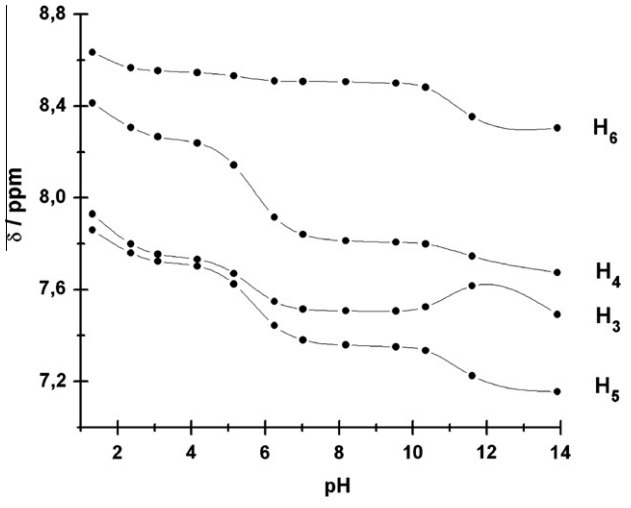


Fig. 5. The chemical shifts of pyridyl protons H_3, H_4, H_5, and H_6 as a function of pH.

In the spectra of ^{13}C NMR 7 resonances is observed (Fig. 7). The methylene C_β resonance splits into a doublet (1:1) by coupling with adjacent P_β nucleus ($^1J_{C\beta-P\beta} = 133.5$ Hz) and splits into a doublet by three-bond coupling with the neighboring $P_{\beta'}$ atom ($^3J_{C\beta-P\beta'} = 4.9$ Hz). The C_α resonance splits into a triplet (1:2:1) by coupling with two equivalent phosphorus ($^3J_{C\alpha-P} = 4.36$ Hz). Both values of $^1J_{C-P}$ and $^3J_{C-P}$ are similar with these observed in ethylenediaminotetra(methylephosphonic) acid (EDTMP) ($^1J_{C-P} = 130.9$ Hz and $^3J_{C-P} = 4.4$ Hz) [17].

In the ^{31}P NMR spectra the resonance line splits into a triplet peak with the intensity 1:2:1 by coupling with two protons H_β of the adjacent methylene groups. The phosphorus resonance line becomes a singlet peak by complete decoupling with the protons and indicates that both phosphonic groups are equivalent.

The observed spectral pattern of studied compound (six resonances in ^1H NMR spectra, one signal in ^{31}P NMR and seven in ^{13}C NMR) indicates that the symmetry of studied molecule is C_S.

The chemical shift of phosphorus signal varies with the pH following an approximately parabolic pattern, due to acid–base equilibria in the aqueous solution (Fig. 8).

The chemical shift of ^{31}P undergoes upfield transition from 17.98 ppm at pH 1.3–6.77 ppm at pH = 8.18 and next a downfield transition at higher pH values of solution. It is caused by the deprotonation of phosphonic groups in the pH range 0–8 and then by probable binding of counteraction(s) such as Na^+, K^+ at higher pH ($\geqslant 8$). On the other hand the influence of deprotonation of N(amino) atoms cannot be excluded due to strong intramolecular hydrogen

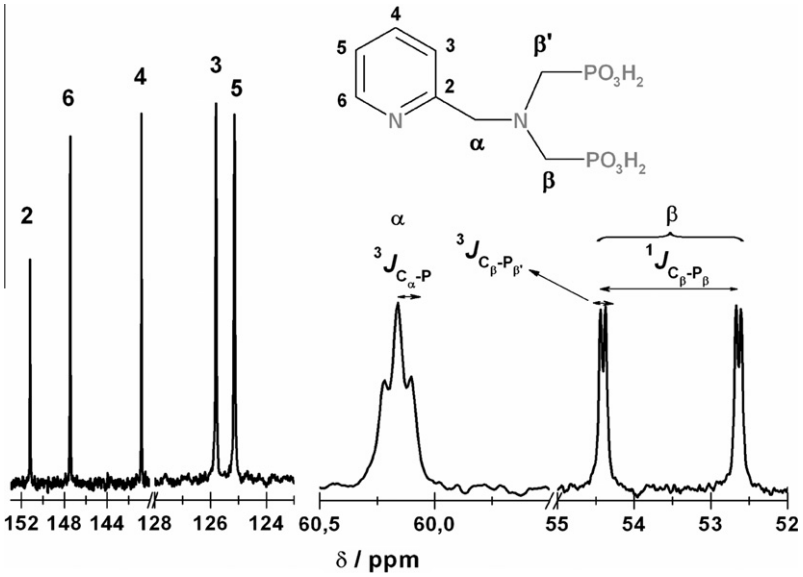


Fig. 7. ^{13}C NMR spectra in D_2O at pH 6.25.

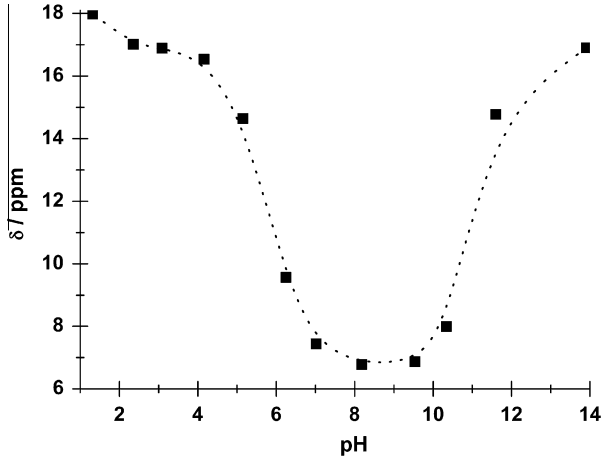


Fig. 8. pH dependence of ^{31}P chemical shift.

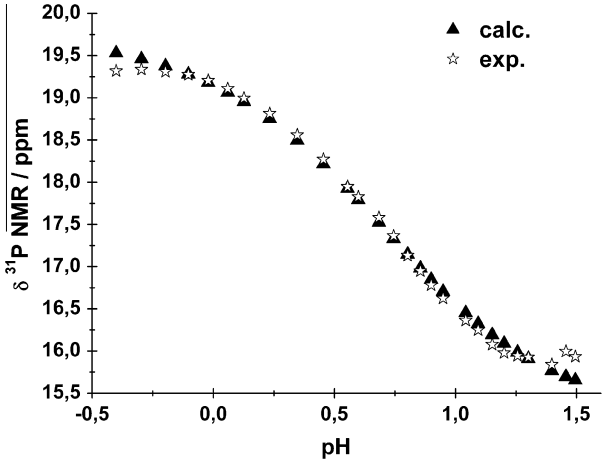


Fig. 9. ^{31}P NMR titration curve of NP_2py.

bonding formation between N(amino) and O(PO_3^{2-}) atoms. This behavior is rather typical for aminophosphonates with N–C–P skeleton [18].

The analysis of the experimental and theoretical electron density distribution studies in aminomethylphosphonates [3] and methylphosphonates [9b] indicates that covalent P–O bonds are highly polarized, moreover the protonation of oxygen atom gives rise to increased polarization of the P–O bond (50% for P–O(deprotonated) and 60% for P–O(H)). Obviously, the protonation of oxygen atom usually causes the elongation of P–O bond (~5% in studied compounds), as it was shown above. The variation of electron density distribution near the P–O bonds results in the change of the phosphorus atom shielding, and consequently changes of P resonance chemical shift. Hence at higher pH of solution the P resonance line shifts to lower fields and the coupling constants $^2J_{H\beta-P}$ increase.

For estimation of the two first dissociation constants the ^{31}P NMR the titration of **V** between pH −0.5 and 1.5 were carried out (Fig. 9).

The total concentration of the salt was 0.011 M. The hydrogen ion concentration was varied by addition of appropriate amount of perchloric acid. It is worth to note that complete dissociation of $HClO_4$ is valid at concentration used in these experiments ($c < 2.5$ M $pK_a \approx -10$) [19]. All solutions were prepared with ionic strength $I = 2.5$ M by the addition of appropriate amounts of $NaClO_4$.

In this pH range the dissociation of two protons from phosphonic group(s) should be expected. The shape of the titration curve strongly suggests that both dissociation constants are very similar.

$$H + L \leftrightarrow HL \quad \beta_1 = \frac{[HL]}{[H] \cdot [L]} = K_1 \tag{1}$$

$$2H + L \leftrightarrow H_2L \quad \beta_2 = \frac{[H_2L]}{[H]^2 \cdot [L]} = K_1 \cdot K_2 \tag{2}$$

The next third dissociation constant for analogous phosphonic compounds is at least one or two orders larger, therefore when calculating the first two dissociation constants the higher ones may be neglected. The minimization the sum of $\sum(\delta_{exp} - \delta_{calc})^2$ using the following Eq. (3) leads to determination of the β_1 and β_2 values.

$$\delta_{calc} = \frac{\delta_L + [H] \cdot \beta_1 \cdot \delta_{HL} + [H]^2 \cdot \beta_2 \cdot \delta_{H_2L}}{1 + [H] \cdot \beta_1 + [H]^2 \cdot \beta_2} \tag{3}$$

Table 3
Protonation and dissociation constants of NP_2py and NTP (nitrilotri(methylphosphonic) acid).

	NP_2py	NTP [11b]
β_1	9.62 ± 0.013	
β_2	48.2 ± 0.012	
pK_{1dis}	0.70 ± 0.03	0.5 ± 0.2–1.1 ± 0.2
pK_{2dis}	0.98 ± 0.05	1.0 ± 0.1–1.2 ± 0.2

The best fit of the data set were obtained for the following chemical shifts of L, HL and H_2L species: δ_L = 15.25 ppm, δ_{HL} = 16.3 ppm and δ_{H_2L} = 19.8. The determined values of β_1 and β_2 are compared in the Table 3. The obtained values of pK_{dys} are close to that for nitrilotris(methylenephosphonic) acid (NTP) reported by Grossmann et al. [11b].

The changes of chemical shift of ^{31}P resonance above pH 1.5 (Fig. 8) indicate that the next steps of **IV** acid deprotonation occur between pH 2–3 and 4–7. Above the pH > 8.2 deprotonation of the phosphonic groups is complete.

3. Conclusions

The structural (X-ray) and spectroscopic (NMR) properties of **V** were investigated. The reported crystal structure results indicate that the studied compound is in the form of diprotonic H_2L acid. Both phosphonic groups are monoprotonated as manifested by elongation of P–OH bond lengths of about 0.07 Å, in comparison with the remaining P–O bonds. The analysis of the nitrogen (N1(amino)) – neighbor atom distances and the network of the hydrogen bonds suggests that the N1(amino) atom is deprotonated. The charge of $[H_2L]^{2-}$ anion is compensated by two ammonium cations.

The NMR studies of aqueous solution of **V** indicate that both phosphonic groups are equivalent and the spectral pattern suggests that the symmetry of the molecule of **IV** is C_s. The studied acid potentially possesses 6 protonation sites (four at oxygen atoms from phosphonic groups and two at nitrogen atoms). Below the pH = −0.5 the H_6L acid is completely protonated. The ^{31}P NMR titration between pH −0.5 and 1.5 indicate that the first two dissociation constants are pK_{1dis} = 0.70 ± 0.03 and pK_{2dis} = 0.98 ± 0.05. These results may suggest that the coordination of synthesised ligand to Ln^{3+} cations may begin around pH 0.5–2.

The next steps of dissociation occur between pH 2–3 and 4–7. Above the pH > 8.2 deprotonation of the phosphonic groups is complete. The observed changes of chemical shifts of pyridyl protons suggest that the deprotonation of pyridyl nitrogen atoms occur between pH 5 and 6.

The increase of the $^2J_{H\beta-P}$ coupling constants together with pH as well as the observed changes of ^{31}P NMR chemical shifts above pH ~8 possibly arise from deprotonation of N(amino) atoms. In spite of that in crystal of **V** the N(amino) atoms are deprotonated in aqueous solution in broad pH range (−0.5 to 10) the N(amino) atoms are protonated; the difference is probably brought about by different conformations of the compound in solution and in the crystalline state.

4. Experimental section

4.1. Synthesis of 2-pyridinealdoxime (II)

Pyridinecarboxaldehyde (I) 2.2 g (0.021 mol) was dissolved in 45 ml of H_2O/CH_3OH 1:2 solution. Next potassium carbonate 1.59 g (0.011 mol) and hydroxylamine hydrochloride 1.45 g (0.021 mol) was added. The mixture was refluxed for 24 h, then the solvent was evaporated under the reduced pressure. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.6 (6), 8.34 (α), 7.82 (3), 7.71 (4), 7.27 (5), ^{13}C NMR ($CDCl_3$, 300 MHz) δ (ppm): 152.0 (2), 149.9 (6), 149.3 (α), 137.7 (4), 124.4 (5), 121.5 (3).

4.2. Synthesis of 2-(aminomethyl)-pyridine(III)

The crude 2-pyridinealdoxime (II) was dissolved in 30 ml of 80% acetic acid, next 6 g of metallic Zn was added and the whole was stirred at ~40 °C for 48 h under reflux. Next the insoluble residue was filtered away and the solution was alkalized to pH ~14 using NaOH, then the amine was extracted using $CHCl_3$ (POCH). Next the amine was extracted using the concentrated hydrochloric acid (36%, POCH). The solution was evaporated under the reduced pressure and the solid residue (crude 2-(aminomethyl)-pyridine hydrochloride) was recrystalised four times from hot ethanol. The yellow white 2-(aminomethyl)-pyridine hydrochloride powder was obtained with the yield 2.99 g, 73%. ^1H NMR (D_2O, 300 MHz) δ (ppm): 8.65 (6), 8.15 (α), 7.71 (3), 7.66 (4), 4.42 (5). $C_6H_{12}N_2$ calc.: C 39.78, H 5.52, N 15.47; found: C 39.1, H 5.2, N 15.7.

4.3. Synthesis of N-(methylene-2-pyridine)-N,N-di(methylenephosphonic) acid (IV)

0.5 g (4.8 mmol) of 2-(aminomethyl)pyridine (AMpy) were mixed together with appropriate amounts of H_3PO_3 (Aldrich) and HCl solution (c_{HCl} ~ 6 M) and heated under the reflux. Next, small portion of paraformaldehyde (Sigma Aldrich) was added. The temperature of reaction was 120–125 °C. The resulting aminomethylphosphonic acid was isolated by standard procedures described in literature [10]. The ^{31}P NMR were used to monitor quantitatively the course of the reaction.

III (mmol)	**H_2CO** (mmol)	**H_3PO_3** (mmol)	Time (h)	Yield (%)	Temp. (°C)
4.8	9.6	9.6	3	45	120–125
4.8	9.6	9.6	24	50	120–125
4.8	14.4	14.4	3	52	120–125
4.8	14.4	14.4	24	57	120–125

4.4. Preparation of crystals (V)

A solution of **IV** was alkalized with $NH_{3(aq)}$ solution to pH around 11. Next the mother solution was evaporated and concentrated to about one-fifth of the staring volume and the hot CH_3OH was added until the resulting precipitate stopped to redissolve. The colorless triangular prisms of $(NH_4)_2(pyCH_2)N(CH_2PO_3H_2)_2$ were formed during slow evaporation of the solution after 2 months. $C_8H_{20}N_4O_6P_2$ calc.: H 6.1, N 17.0, found: H 6.0, N 16.9.

4.5. Single-crystal X-ray diffraction analysis

The appropriate crystal was cut from a larger one and mounted on a Kuma KM4 diffractometer equipped with a CCD counter. The collected data were corrected for polarization, Lorentz, and absorption, the last of which was calculated from the crystal habit that was captured from the photo scans. The structure was solved routinely with direct methods. The positions of the C(methylene)-bonded hydrogen atoms were calculated geometrically, the C-(pyridine), O- and N-bonded H atoms were found from

a difference Fourier map and were refined freely. The refinement was full-matrix with all of the non-H atoms anisotropic. All of the computations were performed with the SHELXS97 and SHELXL97 programs [20]. The molecular graphics were prepared with XP program [21].

4.6. Summary of crystallographic data

$C_8H_{20}N_4O_6P_2$, monoclinic, space group $P2_1/c$, $a = 14.3830(14)$, $b = 8.0306(7)$, $c = 13.2769(15)$ Å, $\beta = 109.802(12)^\circ$, $Z = 4$, $d_{calc} = 1.520\ g\cdot cm^{-3}$, 10183 reflections collected, 3475 unique ($R_{int} = 0.0261$), data/parameters: 3475/237, final R indices ($I\_2\sigma I$): $R_1 = 0.0310$, $wR^2 = 0.0776$, final R indices (all data): $R_1 = 0.0427$, $wR^2 = 0.0803$, goodness of fit: 1.030, highest and deepest residual electron density: $0.45e$ Å^{-3}, $-0.29e$ Å^{-3}.

CCDC – 864221 these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.7. NMR measurements

The spectra of the H_2NP_2py ($c = 5.7$ mM $I = 0.1$ M KCl) in D_2O at different pH values were recorded on a Bruker AMX 300, Bruker Avance 500 MHz and Bruker Avance III 600 MHz at 298 K. 5% H_3PO_4 (POCH) and dioxan in D_2O (Aldrich) solutions were used as an external standards in ^{31}P NMR and ^{13}C NMR measurements, respectively. The pH of solutions was adjusted by addition of HCl (Świerk) or NaOH (POCh). For NMR titrations under conditions of constant volume (2.00 ml) and ionic strength ($I = 2.5$ M, $NaClO_4$) the series of 27 aqueous solutions of IV (0.011 M) contained $\times$ M $HClO_4$, $(2.5 - x)$ M $NaClO_4$ and 0.1 ml D_2O were prepared.

Acknowledgement

This work was supported by MNiSW 2273/M/WCH/12.

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