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Zinc(II) complexes of phosphonic acid analogues of aspartic acid and asparagine

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An analogue of aspartic acid obtained by the replacement of the α-carboxylic group by a phosphonic acid group underwent chemical transformation upon the action of zinc(II) ions under neutral and slightly alkaline conditions yielding, most probably, a cyclic phosphonamidate composed of two ligand molecules. In contrast, an analogue obtained by the replacement of the β-carboxylic group by a phosphonic acid moiety did not undergo such a transformation. In order to determine which structural features are responsible for the observed cyclization a series of aminophosphonic acids was synthesized and their behaviour in zinc(II) solutions studied by means of NMR spectroscopy. Cyclization of 1-aminoalkylphosphonic acids upon the action of zinc(II) ions in neutral and slightly alkaline media seems to be a general property of these acids. The crystal structures of two of the studied compounds were also determined.

Recently we have shown that the analogue of glutamic acid obtained by the replacement of the α-carboxylic by a phosphonic acid group undergoes chemical transformation upon the action of zinc(II) ions under neutral and slightly alkaline conditions yielding, most probably, a cyclic phosphonamidate composed of two ligand molecules.[1] This reaction may be considered as a mimic of biologically important reactions of pentavalent phosphorus acids in which zinc acts either as a Lewis acid accepting a lone electron pair of oxygen from the P=O bond and thus increasing the electrophilicity of the phosphorus atom, or by complexing the amine group of the molecule changing significantly its nucleophilicity. In order to determine which structural features are responsible for the ability of phosphonic acid analogues of acidic amino acids to undergo such a transformation, and especially for a better understanding of the role of the carboxylic group, we have studied the behaviour of analogues of aspartic acid and asparagine in aqueous solutions containing zinc(II) ions.

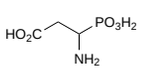
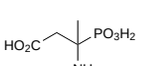
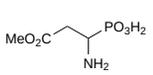
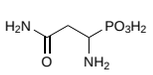
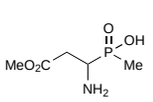
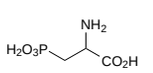
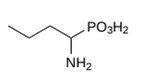
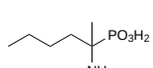
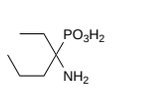
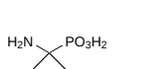
Experimental

Materials

Phosphonic acid analogues of aspartic acid and asparagine as well as their esters were obtained according to previously described procedures.[2] Other aminoalkylphosphonic acids were synthesized according to the standard procedure.[3] All the compounds were used in their racemic forms and are shown in Table 1. The purities and exact concentrations of the solutions of the pro-ligands used for potentiometric studies were determined by the method of Gran.[4] The concentration of zinc(II) chloride stock solution was standardized by complexometric titration with ethylenedinitrilotetraacetate (edta). Carbonate-free potassium hydroxide (the titrant) was prepared and standardized against a standard potassium hydrogenphthalate solution. The concentration of KOH was *ca.* 0.2 mol dm^{-3}.

Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer.

Table 1 Compounds used in this study

Compound	Structure	Name
1		3-Amino-3-phosphonopropionic acid
2		3-Amino-3-phosphonobutyric acid
3		Methyl 3-amino-3-phosphonobutyrate
4		3-Amino-3-phosphonopropionamide
5		Methyl 3-amino-3-[hydroxy(methyl)phosphinoyl]propionate
6		2-Amino-3-phosphonopropionic acid
7		1-Aminobutylphosphonic acid
8		1-Amino-1-methylpentylphosphonic acid
9		1-Amino-1-ethylbutylphosphonic acid
10		1-Aminocyclobutylphosphonic acid

Potentiometric measurements

Acid dissociation constants of the pro-ligands were determined by pH-metric titration of 5 cm^3 samples of concentration 4×10^{-3} mol dm^{-3}. The ionic strength was adjusted to 0.2 mol dm^{-3} with KCl in each case. The titrations were performed over the range pH 2–11.5 with KOH solution of known

concentration (*ca.* 0.3 mol dm^{-3}). All titration solutions were thermostatted at 25 ± 0.1 °C using a constant-temperature water-bath.

The pH was measured with a MOLSPIN automatic titration system using a micro combination pH electrode (Mettler-Toledo, type U402-M6-57/100). The electrode system was calibrated by periodic titrations of HCl solution (3×10^{-3} mol dm^{-3} in KCl) against standard KOH solution. The resulting titration data were used to calculate the standard electrode potentials, $E°$, and the dissociation constant for water ($pK_w = 13.74$). These values were then used to calculate the hydrogen-ion concentration [H^+] from potential readings;[5] number of titrations, 3; calculations, SUPERQUAD computer program.[6]

NMR measurements

Phosphorus and proton NMR spectra were recorded on a Bruker DRX spectrometer operating at 300.13 MHz for ^1H and 121.50 MHz for ^{31}P given in relation to $SiMe_4$ and 85% H_3PO_4, respectively. All downfield shifts are denoted as positive. The Bruker WIN NMR DAISY software was applied to iterate ABCX (X = ^{31}P) ^1H NMR spectra. The J_{HP} and J_{HH} coupling constants obtained in this way were used to calculate rotamer populations.

Samples for NMR studies were prepared in deuteriated water with a pro-ligand concentration of 0.02 or 0.01 mol dm^{-3}. A zinc(II) to pro-ligand molar ratio of 1:2 was applied in all cases using zinc nitrate hexahydrate (Aldrich) as a source of Zn^{II}. The pH of the samples was measured using a Radiometer pHM83 instrument equipped with a 2401C combined electrode and given as meter readings, without correction for pD. The measurements were performed only for freshly prepared samples. This allowed us to avoid among other things extensive hydrolysis of the carboxylate ester functions of compounds **3** and **5**. The hydrolytic cleavage of the CO_2Me group was monitored by integration of the ^1H NMR methyl resonances which corresponded to both CO_2Me and to MeOH which was released upon its hydrolysis. This showed that under the conditions of the experiment the hydrolysis of compound **3** may be neglected, whereas the extent of hydrolysis of **5** increased from about 1% at neutral pH to about 20% at pH 11.6. Under more alkaline solutions only the spectra of 3-amino-3-[hydroxy(methyl)phosphinoyl]butyric acid were recorded. The measurements in solutions containing zinc(II) ions were limited to a rather narrow range of pH (usually between 6–7 and 9.5) because of precipitation.[1]

Crystallography

Crystals of compounds **4** and **10** were obtained by recrystallization from water and were used for the data collection. The space groups and approximate unit-cell dimensions were determined from rotation and Wessenberg photographs. The diffraction data were measured at 293(2) K on a KUMA KM4 computer-controlled four-circle diffractometer with graphite-monochromated Cu-Kα (λ = 1.5418 Å) and Mo-Kα (λ = 0.710 69 Å) radiation respectively.[7]

Details of the diffraction experiments, crystal data collection and refinement are given in Table 3. The structures were solved by direct methods with SHELXS 86[8] and refined on F^2 for compound **4** and F for **10** by full-matrix least-squares methods using SHELXL 93[9] with anisotropic thermal parameters for non-hydrogen atoms. During the refinement an extinction correction was applied but no absorption correction. For compound **4** all hydrogen atoms were found from a Fourier-difference synthesis and refined isotropically. For **10** carbon-bound hydrogen atoms were initially placed in calculated positions (with the thermal parameters being 1.2 times U_{eq} of the parent carbon atom) and the remainder were found from the difference synthesis. Hydrogen atoms of amino groups were refined with isotropic thermal parameters being 1.5 times U_{eq} of the parent nitrogen atom. In the case of compound **10** the absolute structure cannot be determined reliably since the value of the Flack parameter[10] was 0.31(12) and refinement of the inverted structure gave $R = 0.0451$ and $wR = 0.1022$. Scattering factors and real, as well as imaginary, components of anomalous dispersion were those incorporated with SHELXL 93. The ORTEP[11] package was used to generate molecular drawings.

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Table 2 Deprotonation constants (pK) of the studied aminophosphonic acids at 25 °C and $I = 0.2$ mol dm^{-3}. Standard deviations are given in parentheses

	pK		
Compound	NH_3^+	PO_3H^-	CO_2H
1[a]	10.07(1)	5.52	3.44
2	10.82(6)	5.74	3.10
3	9.34(5)	5.40	
4	9.05(5)	5.22	
5	7.4[b]		
6[a]	10.79(1)	6.07	2.40
7	10.03(1)	5.66	
8	10.35(4)	6.02	
9	10.51(4)	6.18	
10	9.79(9)	5.73	

[a] Taken from ref. 12. [b] From NMR measurements; $pK(PO_2H) \approx 1$.

Results

Potentiometric studies of proton complexes

Protonation constants were calculated assuming that ligand concentrations were as calculated from the titration curves and then allowing ligand and proton concentrations to 'float' in SUPERQUAD. It was found that the concentrations never changed by more than 1% and calculated constants remained constant within the calculated errors. This confirmed the purity of the compounds studied.

With the exception of phosphinic acid **5** all the compounds in Table 1 have two common functional groups: amino and phosphonate moieties with some of them having additional groups, namely carboxylic (compounds **1** and **2**), methyl carboxylate (**3**) or amide (**4**) functions. Compounds **2**, **3** and **8** also possess methyl groups in α position in relation to the phosphonic moiety (C_α carbon atom). Since the methyl group is less electronegative than a hydrogen atom, the replacement of the latter by methyl changes the electron density of the C_α carbon atom. This density is partly transferred to the neighbouring nitrogen and phosphorus atoms and consequently the basicity of the NH_3^+ and PO_3H^- groups in compounds **2** and **7** are higher than those found for structurally related compounds **1** and **6** [for example, compare $pK(NH_3^+)$ values for these pairs of compounds in Table 2].

Examination of the $pK(NH_3^+)$ values for compounds **1** and **8** clearly shows that the positioning of the CO_2^- group makes scarcely any difference. Quite oppositely, the presence of a strongly electron-withdrawing methyl carboxylate in β position to an amino moiety (compound **3**) resulted in a significant decrease of $pK(NH_3^+)$. The highest acidity (among phosphonic acids) of the NH_3^+ group observed in the case of compound **4** well illustrates the fact that the inductive effect of an amide group is much greater than that found for methyl carboxylate.

NMR studies

Proton NMR spectra were recorded to obtain populations of rotational isomers for those aspartic acid derivatives which exhibit four-spin ABCX (X = ^{31}P) subspectra. The homo-

Table 3 Homo- (^{1}H–^{1}H) and hetero-nuclear (^{1}H–^{31}P) coupling constants (J/Hz) used in conformational analysis of compounds **4**–**6** and their zinc(II) solutions

	4				Zn^{II}–**4**			**5**			Zn^{II}–**5**		**6**				Zn^{II}–**6**	
pH	0.73	3.27	7.01	11.12	5.02	6.20	9.80	1.03	6.86	11.60	6.58	9.86	1.12	3.12	9.05	12.82	6.68	9.64
^{1}H–^{1}H																		
H^1, H^2	−17.1	−17.0	−17.0	−16.5	−17.0	−16.9	−15.6	−17.7	−17.3	−16.0	−17.4	−16.1	−16.3	−15.7	−14.8	−14.7	−15.5	−15.1
H^1, H^3	10.4	10.8	11.8	11.2	11.0	11.5	11.4	9.8	10.0	11.1	9.9	11.1	8.5	10.8	11.2	11.8	11.6	13.2
H^2, H^3	3.7	3.4	2.8	3.4	3.2	3.0	3.0	4.1	3.9	3.2	3.9	3.3	4.6	3.6	2.2	1.9	2.7	2.1
^{1}H–^{31}P																		
H^1, P	7.5	7.0	5.4	5.5	6.5	6.1	6.0	9.5	7.3	7.1	7.5	7.1	16.0	14.9	12.5	13.5	13.5	11.9
H^2, P	8.8	7.9	6.2	6.5	7.5	6.2	6.4	9.2	8.2	6.9	8.3	6.9	17.7	17.8	16.6	17.7	16.9	17.7
H^3, P	13.9	13.0	12.8	13.3	13.3	13.3	13.6	10.5	9.8	10.3	10.5	10.3	16.1	13.6	11.9	10.0	12.1	11.8

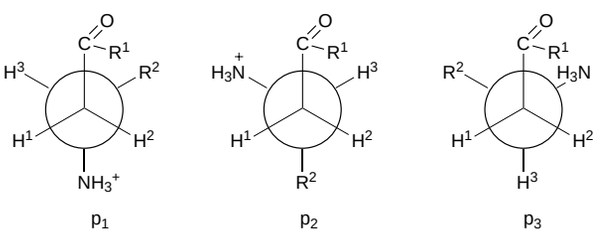


Fig. 1 Newman projections for the three staggered rotamers relative to the $\chi_1[C_\alpha–C_\beta]$ torsion angle (R^1 = OH, R^2 = PO_3H^-, compound **1**; NH_2, PO_3H^-, **4**; OMe, $PMeO_2^-$ **5**)

nuclear J_{HH} and heteronuclear J_{HP} coupling constants used in calculations were obtained by iteration of experimental spectra and representative results are given in Table 3. A conformational analysis of α-aminophosphonic derivatives was performed according to the notation given in Fig. 1 based on $^3J_{HP}$ coupling constants. We have taken two sets of data for calculations, namely J_t = 33.0 Hz and J_g = 4.2 Hz recommended for α-Asp(P) (3-amino-3-phosphonopropionic acid)[12] and the widely used Pachler $^3J_{HH}$ coupling constants (J_t = 13.6 and J_g = 2.6 Hz).[13] Both sets gave, with tolerable precision, approximate values of the mole fraction for each rotamer, as well as showing analogous tendencies in rotamer population changes *versus* pH. Both **4** and **5** adopt, similarly to α-Asp(P),[12] a predominant p_2 conformation, *i.e.* that containing bulky groups located *trans* to each other (Fig. 2). Protonation effects seem to induce particular conformations to a much lesser extent than does steric hindrance (Fig. 2). The intramolecular hydrogen bonding between the protonated amino group and the carbonyl group of the amide, the existence of which was suggested by our crystallographic data, although presumably weaker in solution, may be an additional stabilizing factor which favours the p_2 conformation of **4** over p_2 of **5** at a pH <10.

Among the aminophosphonic acids studied those which are lacking phosphonic and amino groups bonded to the same carbon atom (C_α atom), namely **5** and 2-amino-3-phosphonopropionic acid [β-Asp(P), **6**] seem to belong to the 'fast equilibrium system' class which was discussed in our previous work.[1] In their solutions zinc(II) complexation results only in (dependent on co-ordination) shifting and (dependent on chemical exchange rate) broadening of the single peak in the ^{31}P NMR spectra.

The ^{31}P NMR chemical shift profiles of compound **6** and species formed upon complexation with zinc(II) ions are given in Fig. 3. These data differ significantly from those obtained for the Zn^{II}–γ-Glu(P) 1:2 system [γ-Glu(P) = 2-amino-2-phosphonobutanoic acid] where bidentate chelation involving NH_2 and CO_2^- was shown[1] because β-Asp(P) seems to involve all possible donor groups in zinc(II) co-ordination. This results in five- and six-membered joined chelate rings and a stability

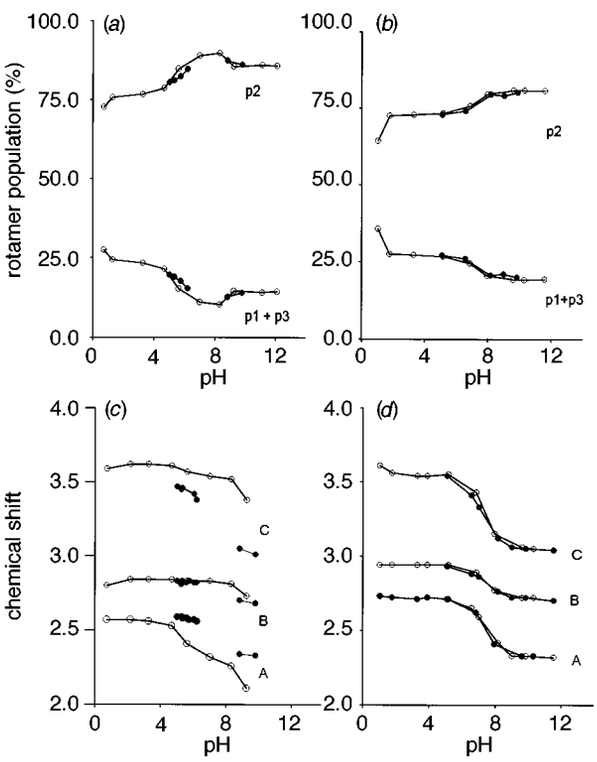


Fig. 2 Rotamer populations and ^{31}P NMR chemical shifts as a function of pH for compounds **4** and **5** and their zinc(II) solutions [(*a*), (*c*) and (*b*), (*d*) respectively]. (○) Free pro-ligands and (●) their zinc(II) solutions

increase of ZnL and ZnL_2 species *versus* the respective Zn^{II}–γ-Glu(P) species of the same stoichiometry.[14] This finding also corresponds fairly well to our general observation that stepwise chelation of zinc(II) by phosphonate followed by complexation by an amino group results both in a gradual downfield shift of ^{31}P resonances and in a significant (about 2–3 log units) decrease in $pK_{NH_3^+}$. Conformational studies of β-Asp(P) were performed using the notation given in Fig. 1 with the replacement of the $CO(R^1)$ group by a phosphonic one (then R^2 corresponds to β-carboxylate). Significant discrepancies were achieved when fractional populations were calculated basing on previously described $^3J_{HH}$ and $^3J_{HP}$ pairs of *trans* and *gauche* coupling constants. As the application of a pair of J_t and J_g values given in this work for vicinal H–P coupling constants seem to be generally restricted to phosphonic derivatives containing a $PCHCH_2$ molecular fragment,[15] we used Pachler's $^3J_{HH}$ *trans* and *gauche* coupling constants.[13] Again, the most stable and sterically favoured conformation of the molecule has a torsion angle χ^1 of 180° (p_2 conformation). However, upon zinc(II) complexation it increased considerably at the expense of

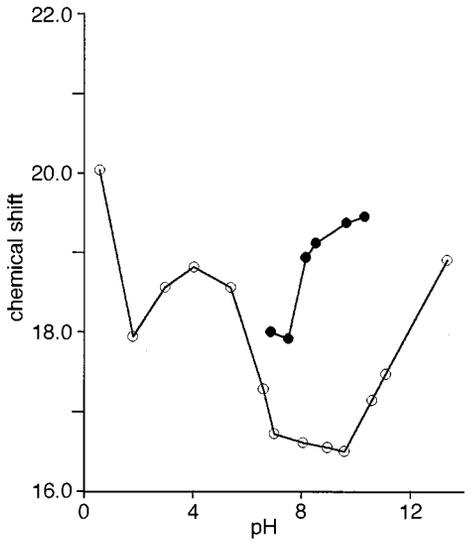


Fig. 3 The ^{31}P NMR chemical shifts as a function of pH for compound **6** (○) and its zinc(II) solutions (●)

both p_1 and p_3. The considerable broadening of the ^{31}P NMR peak in slightly acidic and neutral Zn^{II}–**5** solutions seem to reveal a weak complexation of zinc(II), presumably in a monodentate way *via* the $POMe^-$ group. There is no indication of the involvement of the amino group in metal chelation. As a result no significant chemical shift changes in the ^1H NMR spectra of the pro-ligand solutions upon addition of Zn^{II} (Fig. 2) and invariant rotamer populations in respect of those of the metal-free aminophosphonic acid were observed.

Single ^{31}P NMR resonances were also detected in the Zn^{II}–**4** system at a measurable range of pH values. Extensive precipitation precluded potentiometric measurements at pH > 6.5. The calculations confined to a rather narrow pH range revealed the formation of Zn(HL) ($\log \beta = 11.84$) as a main species at pH 5 with some ZnL ($\log \beta = 5.27$) and ZnL_2 ($\log \beta = 9.30$) complexes which formed stepwise upon increase of pH. Owing to precipitation, NMR data were also restricted to the slightly acidic and alkaline pH regions only (see Fig. 2). Under these conditions distinct differences in chemical shifts of all proton signals *versus* respective free pro-ligand curves seem to reveal a rearrangement of the ligand in the complex where at least the phosphonate and amino groups are involved in co-ordination. Chelation, however, does not significantly influence the rotamer populations with p_2 still being predominant. Extensive precipitation at pH > 6.5 seems to result from formation of a new complex(es) in which all the possible donor groups, including amidate, as described,[16] may be co-ordinated. The above finding corresponds well to our observations considering the Zn^{II}–Met(P) system [Met(P) = 1-amino-4-thiapentylphosphonic acid] where the involvement of thioether sulfur as a third donor group also resulted in formation of poorly soluble zinc(II) complex(es).[17] The IR spectrum of the precipitate did not allow us to determine if this is a zinc(II) complex of unchanged ligand or a complex of its dimeric cyclic form (see Discussion).

The ^{31}P NMR spectra of zinc(II) solutions with compound **1** resemble those recorded for zinc(II) solutions with its homologue, α-Glu(P) [4-amino-4-phosphonobutanoic acid], and structurally related compounds recently studied in our laboratories.[1] In the presence of zinc(II) ions a pair of single resonances appears under neutral and slightly alkaline solutions. The first one, sharp and shifted downfield, remains almost intact with change in pH. The second, broader and appearing at higher field, moves gradually when the pH increases (Fig. 4). The details of these solution equilibria were discussed in our previous paper.[1] A downfield signal was ascribed to a cyclic phosphonamidate formed from the respective pro-

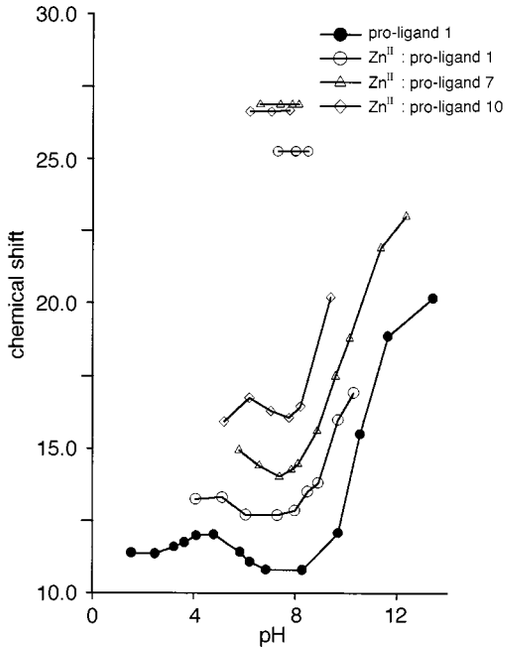


Fig. 4 The ^{31}P NMR chemical shifts as a function of pH for zinc(II) solutions of compounds **1**, **7** and **10**

ligand upon action of zinc(II). If so, similar effects should be observed in spectra of simple α-aminophosphonic acids. Indeed, nearly identical spectra were observed in zinc(II) solutions with compounds **7** and **10**. The assumption of the formation of a cyclic phosphonamidate is strongly supported by the fact that ^{31}P chemical shifts recorded for the new species are always in the range δ 24–29, which is characteristic for phosphonamidates.[18] The pH-dependent ^{31}P resonance might reflect both deprotonation of the amino group and its involvement in stepwise chelation of metal ion. The apparent narrowing of the signal upon increasing temperature reveals an increasing exchange rate between zinc(II) species and pro-ligand, in relatively fast equilibrium. The extent of broadening seems to depend on the structurally related flexibility of the side chain of the respective phosphonic acid and decreases in the following order: pro-ligand **10** ⩾ **7** > **1**. Precipitation of solid material from neutral or slightly alkaline solutions of Zn^{II}–**10** upon standing was observed. This resulted in disappearance of downfield resonances for the samples. Significant narrowing and upfield shifting (≈1.5 ppm) of the second ^{31}P NMR signal which accompanied this process reflects the pH decrease arising from reestablishment of the equilibrium towards the pro-ligand. Examination of the IR spectrum of the precipitated material also supports the formation of a cyclic phosphonamidate: especially in the δ_{NH} region because three peaks (1638, 1615 and 1538 cm^{-1}) present in the spectrum of the pro-ligand are replaced by a single peak at 1590 cm^{-1} in the spectrum of the precipitate. Thus, the precipitate most probably represents the complex of zinc(II) and a cyclic phosphonamidate.

The ^{31}P NMR spectra recorded for respective solutions containing zinc(II) complexes of compounds **2** and **3** contained quite complicated multiplets instead of the single additional downfield resonance characteristic for Zn^{II}–α-Glu(P) and analogous systems. We assume that this feature arises from conformational strain induced by the methyl group in the α position and the rotational barrier at the C_α–C_β bond. In order to verify this assumption the spectra for zinc(II) complexes of compounds **8**, also containing a methyl group at the α position, and **9**, containing an ethyl group at this position, were recorded. Their spectra in neutral and slightly alkaline solutions were similar to those observed for **2** and **3**. The extent of multiplet complexity seems to depend on the size of the alkyl substituent

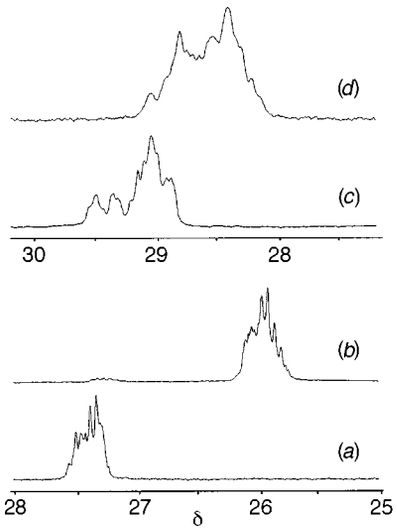


Fig. 5 Low-field ^{31}P NMR resonances of Zn^{II}: pro-ligand 1:2 solutions: (*a*) pro-ligand **2**, pH 7.64; (*b*) **3**, 7.36; (*c*) **8**, 7.45 and (*d*) **9**, 7.47

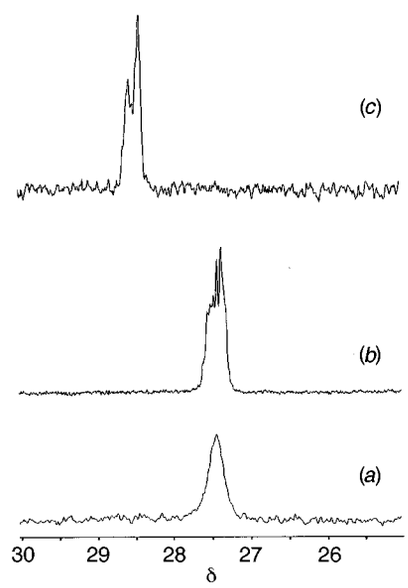


Fig. 6 Low-field ^{31}P NMR resonances of Zn^{II}: pro-ligand 1:2 solutions *versus* temperature: (*a*) pro-ligand **2** at 350 K, pH 7.10; (*b*) at 300 K (after cooling); (*c*) **3** at 350 K, pH 7.36

and somewhat on the length of the aminophosphonic acid backbone (Fig. 5). On the other hand no influence of this type of substitution on upfield resonances was observed. These resonances arise from the complexes of unchanged pro-ligand with zinc(II) ions and their shapes and δ_P values reflect both chemical exchange rates and pH-dependent equilibria between zinc(II)-bonded species and the respective pro-ligand. An increase in temperature caused not only narrowing of upfield resonances but also changed the multiplicity of downfield ^{31}P signals (Fig. 6). In the case of zinc(II) solutions containing pro-ligands **2** and **3** which differ only in carboxylic (free or substituted) functions the signals merged into a single broad peak, whereas for two other α-aminophosphonic acids (pro-ligands **8** and **9**) complete coalescence was not observed even at 350 K. It is worth emphasizing that this process was fully reversible as the ^{31}P NMR spectra recorded after cooling of the parent samples to room temperatures were identical with those initially measured. Again, solid precipitated from Zn^{II}–pro-ligand **9** solutions of initial pH *ca.* 7 upon standing and this resulted in the disappearance of downfield resonances for the remaining solutions. Similarly, as in the case of compound **10**, the IR spectrum

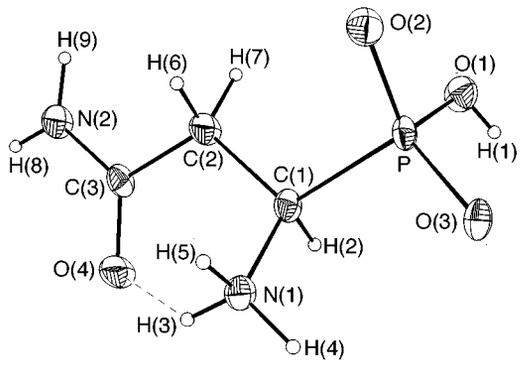


Fig. 7 Molecular structure of 3-amino-3-phosphonopropionamide showing the atomic numbering. Displacement ellipsoids are drawn at the 35% probability level. The intramolecular hydrogen bond is shown as a dashed line

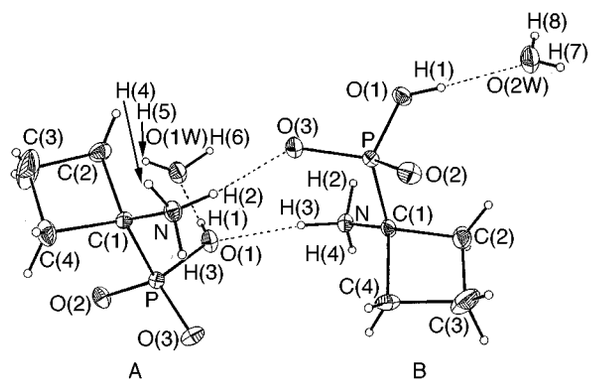


Fig. 8 Molecular structure of two 1-aminocyclobutylphosphonic acid molecules (**A** and **B**) in the asymmetric unit, showing the numbering scheme. Ellipsoids are at the 30% probability level. Hydrogen bonds are shown as dashed lines

of the precipitate strongly supports the suggestion that the downfield resonance represents a complex between zinc(II) and a cyclic phosphonamidate. Also in this case changes in the δ_{NH} region are the most striking since three peaks found in the pro-ligand spectrum (1640, 1615 and 1537 cm^{-1}) are replaced by a single peak at 1579 cm^{-1} in the spectrum of the precipitated complex.

Crystal structures

The molecular structure and atom numbering of compounds **4** and **10** are shown in Figs. 7 and 8 respectively. Selected bond distances and angles are given in Table 5. As can be seen in Fig. 7 the phosphonic acid group of compound **4** is ionized with the proton being transferred to the amino group which results in the formation of a zwitterion. The bond lengths and angles in the aminomethylphosphonic acid part of the molecule are in good agreement with those found earlier for [α-Asp(P), compound **1**],[15] and β-Asp(P), **6**.[19] In the present structure two of the three P–O bonds lengths of 1.495(1) and 1.506(1) Å are significantly shorter than the third [1.569(1) Å]. Thus, as in the case of α- and β-Asp(P), the two shorter P–O bonds may have partially double-bond character, while the longer one corresponds to the P–OH bond. The P–C(1) distance of 1.845(2) Å is slightly longer than the P–CH_2 bond in β-Asp(P) [1.809(4) Å] and similar to that found in α-Asp(P) [1.846(4) Å].

Compound **4** is planar with the maximum deviation from the least-squares best plane through atoms P(1), C(1), C(2) and C(3) being only 0.004(1) Å, while N(1) and N(2) show deviations of −1.166(4) and 0.070(4) Å, respectively. The amide moiety is also planar; the maximum deviation from the best plane through N(2), C(3), O(4) and C(2) is 0.001 Å. The hydrogen atoms H(8) and H(9) lie close to this plane [0.01(2) and

Table 4 Summary of crystal data, data collection and refinement conditions for compounds **4** and **10**

	4	**10**
Formula	$C_3H_9N_2O_4P$	$C_4H_{10}NO_3P{\cdot}H_2O$
M	168.09	169.12
Crystal symmetry	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbc2_1$
No. reflections (2θ/°)	25 (25–37)	45 (20–29)
a/Å	8.455(2)	6.368(2)
b/Å	9.600(2)	20.093(2)
c/Å	8.930(2)	11.700(4)
β/°	110.64(3)	
U/Å^3	678.3(3)	1497(6)
Z	4	8
D_c/g cm^{-3}	1.646(1)	1.501(1)
D_m/g cm^{-3} [b]	1.65	1.50
F(000)	352	720
Crystal dimensions/mm	0.25 × 0.20 × 0.18	0.35 × 0.30 × 0.30
Decay of standards (%)	2	2.5
Reflections measured	1521	3554
2θ Range/°	10–161.0	5.0–62.0
h,k,l Ranges	0–10, 0–11, −11 to 10	0–8, 0–26, −15 to 15
Reflections observed [$F_o \geqslant 4\sigma(F)$]	1273	2458
μ/mm^{-1}	3.372	0.328
Extinction correction	0.0030(8)	0.0050(12)
No. parameters varied	124	230
Weights (a, b, f) [c]	0.0803, 0.26, 1/3	0.0, 1.05, 1/3
Goodness of fit	1.065	1.077
$R1 = \Sigma(\|F_o\| - \|F_c\|)/\|F_o\|$	0.0367	0.044
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$	0.1076	0.0991
Largest feature in final difference map/e Å^{-3}	0.35, −0.25	0.35, −0.29

[a] Details in common: three standard reflections every 100; Lorentz-polarization correction; ω–2θ scans. [b] By flotation in chlorobenzene–carbon tetrachloride. [c] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [f{\cdot}\max(0 \text{ or } F_o^2) + (1 - f)F_c^2]$.

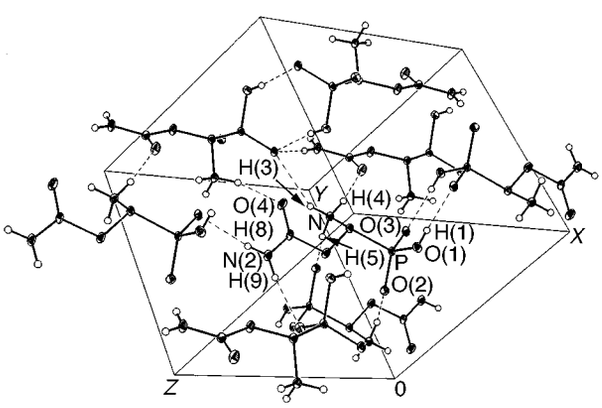


Fig. 9 Crystal-packing arrangement of compound **4**. Hydrogen bonds are shown as dashed lines

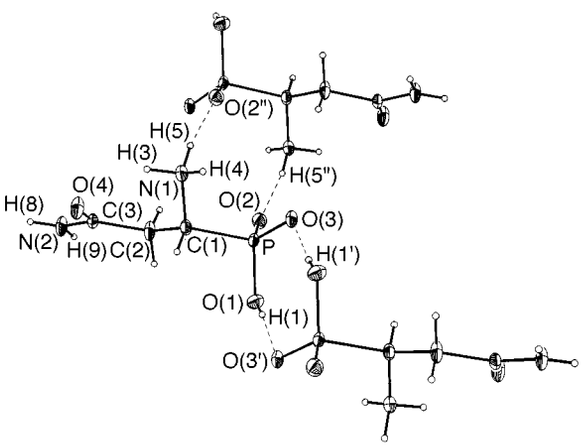


Fig. 10 View of dimers of compound **4** showing the atomic numbering. Displacement ellipsoids are at the 30% probability level. The intramolecular hydrogen bond is shown as a dashed line. Primed atoms (′, ″) and all other atoms in the same molecules are at equivalent positions $1 - x$, $1 - y$, $-z$ and $-x$, $1 - y$, $-z$

0.06(3) Å]. The observed N(2)–C(3) value of 1.323(2) Å is intermediate between a double and a single bond and compares well to the values for analogous bonds in other compounds.[20] The carbonyl C=O double bond [1.234(3) Å] is significantly longer than the normal length (1.215 Å) and agrees well with the length expected when the O atoms take part in hydrogen-bond formation.[21] This is the case here since O (carbonyl) is an acceptor of two hydrogen bonds [2.756(2) and 2.788(2) Å] from two hydrogen atoms from the N(1) amino groups.

The side-chain conformation is given by the P–C–C–C and N–C–C–C torsion angles (Table 6), 179.5(1) and −57.1(2)°. The same conformation was found for α-Asp(P), for which the corresponding angles are 176.5(3) and −60.0(4)°. The HO(1)–P(1)–C(1)–C(2) torsion angle is however of −79.8(1)°, differing by about 11° from that observed in α-Asp(P) [91.1(3)°].

An extensive hydrogen-bond network exists in the crystal structure of compound **4** (Table 7 and Fig. 9) involving all the phosphonic, amine and amide groups. The conformation of the molecule is stabilized by the formation of an intramolecular N(1)–H(3)···O(4) hydrogen bond of 2.756(2) Å. In addition, H(3) participates in a second weak hydrogen bond [3.257(2) Å] involving atom O(3) of the phosphonic group from a neighbouring molecule. Furthermore, a slightly longer hydrogen bond [2.904(2) Å] occurs between N(2)–H(9) and O(2). On the other hand, adjacent molecules are held together by pairs of O(1)–H(1)···O(3) [2.584(2) Å] and N(1)–H(5)···O(2) [2.693(2) Å] hydrogen bonds related by two centres of symmetry from centrosymmetric dimers (Fig. 10). All dimers in the crystal are connected to each other *via* the linear N(2)–H(8)···O(3) [2.993(2) Å] hydrogen-bond system in which the amide group acts as a donor and the phosphonic oxygen O(3) at x, y, $1 + z$ is an acceptor.

In the solid state compound **10**, similarly to other aminophosphonates, exists as a zwitterion. The asymmetric unit of its hydrate which comprises two independent molecules (**A** and **B**) and two water molecules is shown in Fig. 8 with the atomic

Table 5 Selected bond lengths (Å) and angles (°) for compounds **4** and **10**

Compound **4**			
P–O(2)	1.495(1)	N(1)–C(1)	1.488(2)
P–O(3)	1.506(1)	N(2)–C(3)	1.323(2)
P–O(1)	1.569(1)	C(1)–C(2)	1.519(2)
P–C(1)	1.845(2)	C(2)–C(3)	1.517(2)
O(4)–C(3)	1.234(3)		
O(2)–P–O(3)	117.5(1)	N(1)–C(1)–P	110.7(1)
O(2)–P–O(1)	106.9(1)	C(2)–C(1)–P	111.0(1)
O(3)–P–O(1)	112.0(1)	C(3)–C(2)–C(1)	113.4(2)
O(2)–P–C(1)	109.4(1)	O(4)–C(3)–N(2)	123.5(2)
O(3)–P–C(1)	107.6(1)	O(4)–C(3)–C(2)	120.4(2)
O(1)–P–C(1)	102.9(1)	N(2)–C(3)–C(2)	116.1(2)
N(1)–C(1)–C(2)	110.8(1)		
Compound **10**			
Molecule **A**		Molecule **B**	
P(1A)–O(1A)	1.579(3)	P(1B)–O(1B)	1.579(3)
P(1A)–O(2A)	1.496(3)	P(1B)–O(2B)	1.489(3)
P(1A)–O(3A)	1.495(3)	P(1B)–O(3B)	1.495(3)
P(1A)–C(1A)	1.821(5)	P(1B)–C(1B)	1.802(6)
N(1A)–C(1A)	1.481(6)	N(1B)–C(1B)	1.510(7)
C(1A)–C(2A)	1.561(7)	C(1B)–C(2B)	1.531(7)
C(1A)–C(4A)	1.548(7)	C(1B)–C(4B)	1.548(6)
C(2A)–C(3A)	1.481(8)	C(2B)–C(3B)	1.531(9)
C(3A)–C(4A)	1.467(9)	C(3B)–C(4B)	1.511(9)
O(1A)–P(1A)–O(2A)	111.4(2)	O(1B)–P(1B)–O(2B)	111.7(2)
O(1A)–P(1A)–O(3A)	106.0(2)	O(1B)–P(1B)–O(3B)	106.1(2)
O(1A)–P(1A)–C(1A)	104.9(2)	O(1B)–P(1B)–C(1B)	103.9(2)
O(2A)–P(1A)–O(3A)	118.9(2)	O(2B)–P(1B)–O(3B)	118.6(2)
O(2A)–P(1A)–C(1A)	107.4(2)	O(2B)–P(1B)–C(1B)	107.1(2)
O(3A)–P(1A)–C(1A)	107.4(2)	O(3B)–P(1B)–C(1B)	108.5(2)
P(1A)–C(1A)–N(1A)	111.4(2)	P(1B)–C(1B)–N(1B)	110.5(3)
P(1A)–C(1A)–C(2A)	115.4(3)	P(1B)–C(1B)–C(2B)	114.9(4)
P(1A)–C(1A)–C(4A)	114.7(3)	P(1B)–C(1B)–C(4B)	116.6(4)
N(1A)–C(1A)–C(2A)	113.5(4)	N(1B)–C(1B)–C(2B)	113.5(4)
N(1A)–C(1A)–C(4A)	112.8(4)	N(1B)–C(1B)–C(4B)	110.7(4)
C(2A)–C(1A)–C(4A)	87.1(4)	C(2B)–C(1B)–C(4B)	89.1(4)
C(1A)–C(2A)–C(3A)	89.0(5)	C(1B)–C(2B)–C(3B)	88.2(5)
C(2A)–C(3A)–C(4A)	93.4(6)	C(1B)–C(3B)–C(4B)	90.5(4)
C(1A)–C(4A)–C(3A)	90.3(5)	C(1B)–C(4B)–C(3B)	88.3(4)

numbering schemes. The two molecules are rather similar, but not identical (Table 5). The bond lengths and angles of the phosphonic groups are very similar to each other in both structures. The main differences are found in the cyclobutyl rings. Bonds C(3)–C(2) and C(3)–C(4) appear to be shorter in molecule **A** and in **B** whereas the C(2)–C(3)–C(4) angles in the two molecules differ by 3.0°. The calculated values of the bonds and angles in which atom C(3A) is involved should be taken, however, with some reservation, because of the larger displacement parameter found for this atom (Fig. 8).

The four-membered ring of molecule **A** is in a different conformation from that of **B**. The amount of puckering defined as the angle between the planes C(2)–C(1)–C(4) and C(2)–C(3)–C(4) is 5.8(4)° for **A** and 21.4(5)° for **B**. This indicates that the cyclobutane ring of **A** has an approximately planar conformation. The angles of bonds around atoms C(1) vary from 87.1(4) to 115.4(3)° (for **A**) and 89.1(4) to 116.6(4)° (for **B**) and the geometry around C(1) in both molecules is typical for a four-membered ring.[22]

As in other aminophosphonic acids, compound **10** also manifests the characteristic feature of a network of intermolecular hydrogen bonds (Table 7). Hydrogen bonds exist between the crystallographically independent acid molecules. Thus, molecules **A** and **B** of the asymmetric unit are interconnected by two hydrogen bonds, which involve the hydrogen atoms of amino groups and the phosphonic oxygen atoms (Fig. 8). The phosphonic groups of the two forms of **10** participate in

Table 6 Selected torsion angles (°) for compounds **4** and **10**

Compound **4**	
O(2)–P–C(1)–N(1)	−89.9(1)
O(3)–P–C(1)–N(1)	38.3(1)
O(1)–P–C(1)–N(1)	156.7(1)
O(2)–P–C(1)–C(2)	33.6(2)
O(3)–P–C(1)–C(2)	161.8(1)
O(1)–P–C(1)–C(2)	−79.8(1)
N(1)–C(1)–C(2)–C(3)	−57.1(2)
P–C(1)–C(2)–C(3)	179.5(1)
C(1)–C(2)–C(3)–O(4)	3.3(3)
C(1)–C(2)–C(3)–N(2)	−176.7(2)
Compound **10**	
O(2A)–P(1A)–C(1A)–N(1A)	164.2(3)
O(3A)–P(1A)–C(1A)–N(1A)	35.2(3)
O(1A)–P(1A)–C(1A)–N(1A)	−77.3(3)
N(1A)–C(1A)–C(2A)–C(3A)	−117.7(6)
N(1A)–C(1A)–C(4A)–C(3A)	118.4(7)
C(4A)–C(1A)–C(2A)–C(3A)	−4.0(7)
C(1A)–C(2A)–C(3A)–C(4A)	4.2(7)
C(2A)–C(3A)–C(4A)–C(1A)	−4.2(7)
C(2A)–C(1A)–C(4A)–C(3A)	4.0(7)
O(2B)–P(1B)–C(1B)–N(1B)	168.6(3)
O(3B)–P(1B)–C(1B)–N(1B)	39.5(3)
O(1B)–P(1B)–C(1B)–N(1B)	−73.1(3)
C(4B)–C(1B)–C(2B)–C(3B)	−14.8(5)
C(1B)–C(2B)–C(3B)–C(4B)	15.2(5)
C(2B)–C(3B)–C(4B)–C(1B)	−15.0(5)
C(2B)–C(1B)–C(4B)–C(3B)	15.0(6)
N(1B)–C(1B)–C(4B)–C(3B)	129.9(5)
N(1B)–C(1B)–C(2B)–C(3B)	−127.1(5)

Table 7 Hydrogen bond lengths (Å) and angles (°) for compounds **4** and **10**

D–H···A	D···A	D–H	H···A	D–H···A
Compound **4**				
O(1)–H(1)···O(3^{I})	2.584(2)	0.71(3)	1.88(2)	172(2)
N(1)–H(3)···O(4)	2.756(2)	0.88(3)	2.06(3)	136(2)
N(1)–H(3)···O(3^{II})	3.257(2)	0.88(3)	2.57(3)	136(2)
N(1)–H(4)···O(4^{II})	2.788(2)	0.91(3)	1.90(3)	167(2)
N(1)–H(5)···O(2^{III})	2.693(2)	0.98(3)	1.73(3)	169(2)
N(2)–H(8)···O(3^{IV})	2.993(2)	0.83(3)	2.17(3)	171(2)
N(2)–H(9)···O(2^{V})	2.904(2)	0.88(3)	2.03(3)	172(2)

Symmetry codes: I $1-x, 1-y, -z$; II $x, \frac{3}{2}-y, -\frac{1}{2}+z$; III $-x, \frac{3}{2}-y, -\frac{1}{2}+z$; IV $-x, 1-y, -z$; V $x, y, 1+z$; VI $x, \frac{1}{2}-y, \frac{1}{2}+z$.

Compound **10**

Molecule **A**

N(1A)–H(2A)···O(3B)	2.706(5)	0.84(6)	1.87(6)	173(5)
N(1A)–H(3A)···O($1B^{I}$)	2.756(5)	0.91(6)	2.10(6)	157(5)
N(1A)–H(4A)···O($2A^{II}$)	2.800(5)	0.86(6)	1.95(6)	176(6)
O(1W)–H(5)···O($3B^{III}$)	2.776(6)	0.76(6)	2.07(7)	156(5)
O(1W)–H(6)···O($2A^{IV}$)	2.813(5)	0.93(6)	1.87(6)	173(6)
O(1A)–H(1A)···O(1W)	2.571(5)	0.74(5)	1.83(6)	173(6)

Molecule **B**

N(1B)–H(2B)···O($3A^{IV}$)	2.752(5)	0.96(6)	1.83(6)	159(5)
N(1B)–H(3B)···O(1A)	2.877(5)	0.96(5)	1.97(6)	157(5)
N(1B)–H(4B)···O($2B^{V}$)	2.813(5)	0.81(6)	2.02(6)	167(5)
O(2W)–H(7)···O($3A^{VI}$)	2.767(6)	0.74(7)	2.14(6)	162(5)
O(2W)–H(8)···O($2B^{IV}$)	2.778(5)	0.83(6)	1.97(6)	166(5)
O(1B)–H(1B)···O(2W)	2.580(5)	0.78(6)	1.81(5)	173(5)

Symmetry codes: I $x-1, y, z$; II $x, \frac{1}{2}-y, -\frac{1}{2}+z$; III $x, \frac{1}{2}-y, \frac{1}{2}+z$; IV $1+x, y, z$; V $1-x, 1-y, \frac{1}{2}+z$; VI $1-x, 1-y, -\frac{1}{2}+z$.

an additional hydrogen bond with the phosphonic acid groups of the other molecules and with the water oxygen atoms, O(1W) and O(2W). Thus, water forms three hydrogen bonds: two as a donor with phosphonate atoms O(3) and O(2), and a very short one as an acceptor with O(1). Consequently, compound

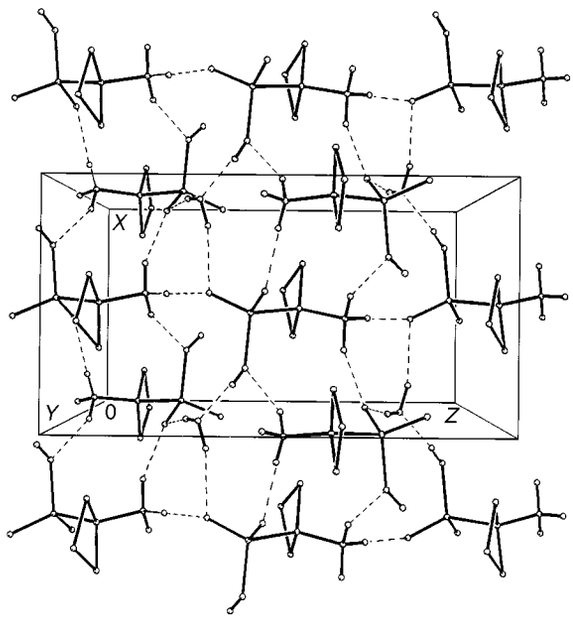
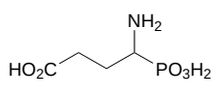


Fig. 11 Crystal-packing arrangement of compound **10**. Hydrogen bonds are shown as dashed lines



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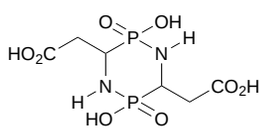

12

10 forms a channel-like structure in which water molecules lie in hydrophilic channels surrounded by phosphonic groups. These hydrophilic regions are separated from each other by hydrophobic regions composed of a network of cyclobutyl rings (Fig. 11).

Discussion

In a previous study we found that the analogue **11** obtained by the replacement of the α-carboxylic group of glutamic acid by a phosphonic acid moiety underwent chemical transformation upon action of zinc(II) ions under neutral or slightly alkaline conditions, yielding most probably a cyclic phosphonamidate **12** composed of two ligand molecules.[1] In order to determine which structural features are responsible for the formation of this cyclic product we have undertaken similar studies using phosphonic acid analogues of asparagine and aspartic acid as pro-ligands. They were chosen intentionally as shorter homologues of compound **11** which should provide sterically hindered cyclic phosphonamidates. As seen from NMR studies, phosphonic acid analogues of aspartic acid exhibit an identical pattern of reactivity upon action of zinc(II) ion in neutral and alkaline media. Thus, compound **6** obtained by the replacement of the β-carboxylic moiety in aspartic acid by a phosphonic acid group did not undergo this transformation as indicated by the existence of only one signal in the ^{13}P NMR spectra of its solutions with zinc(II). Quite oppositely, the spectra of zinc(II) solutions of compound **1**, obtained by replacement of the α-carboxylate moiety of aspartic acid, resemble those recorded for zinc(II) solutions with its homologue (**11**) since a pair of single resonances appears in neutral and slightly alkaline solutions. Introduction of a methyl group in the α position of this compound afforded **2** which showed quite complex multiplets instead of the single additional downfield resonance characteristic for compounds **1** and **11**. We assumed that this feature arises from conformational strain induced by the methyl group and the rotational barrier at the C_α–C_β bond resulting in the appearance of various stereoisomers in the ^{31}P NMR spectra. Esterification of compound **2** gave **3** with ^{31}P NMR spectra which are very similar to those obtained for its parent **2**. This suggested that the carboxylic group is not an essential feature for cyclization of aminophosphonates upon action of zinc(II). In order to check this assumption we synthesized a series of simple 1-aminoalkylphosphonic acids **7**–**10** and studied their behaviour in aqueous solutions containing zinc(II). The ^{31}P NMR spectra of compound **7** observed in zinc(II) solutions were nearly identical with those observed for **1**, indicating that the formation of a cyclic phosphonamidate is independent of the presence of an additional carboxylate moiety in the aminophosphonate side-chain. Consequently the spectra of zinc(II) solutions of compounds **8** and **9** are very similar to those observed for **2** and **3**. Thus, a complex pattern of downfield resonances, arising from the formation of cyclic compounds characterized by conformational strain induced by the substituent at the α position and the rotational barrier at the C_α–C_β bond, was found. Additional proof of the importance of this rotational barrier comes from the spectra of compound **10**. This highly symmetric compound gave spectra identical with those recorded for the analogue **1**, namely a pair of single resonances appears in neutral and slightly alkaline solutions.

Among analogues in which an α-carboxylate moiety was replaced by a phosphonic acid group only compounds **4** and **5** gave only one peak in their ^{13}P NMR spectra with zinc(II) ion. This indicates that the replacement of a phosphonate moiety by a methyl group completely suppresses the formation of the cyclic phosphonamidate. Compound **4**, however, should undergo such a cyclization. It may be suppressed by a massive crystallization of its zinc(II) complex from the solutions at pH > 6.5.

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