Aminomethylenephosphinic Acids and their Complexing Properties†

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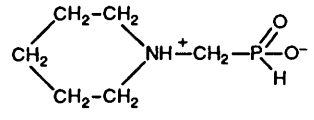
A study of the dependence of the ^1H, ^{31}P and ^{13}C NMR spectra of D_2O solutions of piperidinomethylphosphinic acid (HL^1) and piperazine-1,4-diylbis(methylene)bis(phosphinic acid) (H_2L^2) on the pH has indicated a strong acidity of the phosphinic groups and a low basicity of the nitrogen atoms. It is confirmed that the acids form zwitterions in aqueous solution and that the HL^1 ring behaves similarly to the *N*-methylpiperidine ring. The stability constants of complexes formed with Mg^{2+}, Ca^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} are lower than those of their acetic or phosphonic acid analogues. In the solid state, $HL^1 \cdot H_2O$ exists as a zwitterion, monoclinic, space group $P2_1/n$, a = 6.884(2), b = 11.485(2), c = 11.994(2) Å and β = 97.87(2)°. Two molecules are linked by hydrogen bonds into dimers which are connected by water molecules to form endless chains.

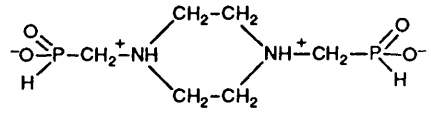
Aminomethylene-phosphinic and -phosphonic acids are phosphorus analogues of the better known aminocarboxylic acids. While aminomethylenephosphonic acids have been studied widely, fewer papers have dealt with the co-ordination properties, in solution [1–4] and in the solid state,[5–9] of phosphinic acids $>NCH_2-P(R)O_2H$ and only two [2,4b] when R = H.

It has been found so far that, compared with aminomethylenephosphonic and aminocarboxylic acids, the nitrogen atoms of aminomethylenephosphinic acids are very weakly basic and the phosphinic group is often too acidic for potentiometric measurements of pK_A. The complexes have much lower stability constants.[1–4]

In addition to the phosphinic analogues of amino acids and common complexones mentioned above there has been considerable interest in studying their azacycles.[10] This paper reports the first part of a study of polyazamethylenephosphinic acids. The two acids employed were chosen as the simplest model compounds.



Piperidinomethylphosphinic acid
HL^1



Piperazine-1, 4-diylbis(methylene)bis(phosphinic acid)
H_2L^2

Results and Discussion

Structure of $HL^1 \cdot H_2O$.—The present structure of HL^1 is the first reported for an aminomethylenephosphinic acid with a P–H bond. In the crystalline state, $HL^1 \cdot H_2O$ exists as a zwitterion, as shown in Fig. 1. Table 1 lists the atomic coordinates and Table 2 selected bond distances and angles. The two HL^1 molecules are linked through the centre of symmetry by an asymmetric hydrogen bond of the type N–H ··· O with N ··· O 2.710(6) Å. The atoms P, C(1), N, H(n), O(1^{II}), P^{II}, C(1^{II}), N^{II}, H(n^{II}) and O(1) form a non-planar, ten-membered ring which has a chair conformation, in a similar way as does aminomethyl(methyl)phosphinic acid.[11]

The co-ordination around the P atom significantly departs from a regular tetrahedron. The P–O lengths correspond to double-bond character and the difference of 0.02 Å is probably caused by the different types of hydrogen bonds. The O(1)–P–O(2) bond angle of 119.9(1)°, which is substantially larger than the tetrahedral angle, can be attributed to repulsion between O(1) and O(2) and a smaller steric hindrance of H(p). The C–N, P–C and N–H bond distances are in a good agreement with values found for this type of compound.[11,12] The piperidine ring has a chair conformation with $CH_2PO_2H^-$ in the equatorial position.

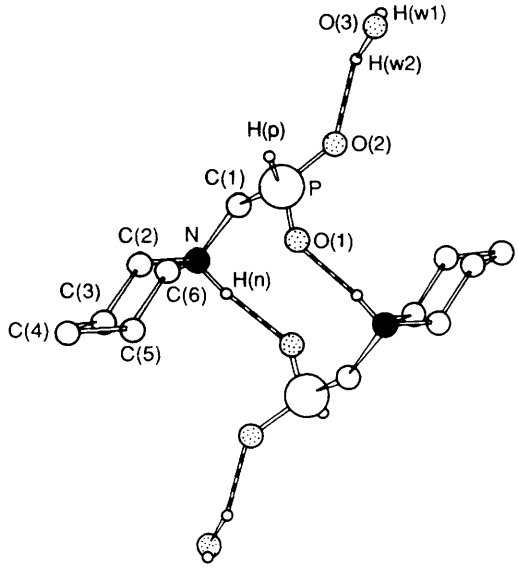


Fig. 1 Perspective view of the $HL^1 \cdot H_2O$ dimer with the atom numbering scheme

The HL^1 dimers form endless chains which are linked by

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx xxv.

Table 1 Atomic coordinates ($\times 10^4$) for non-H atoms of $HL^1 \cdot H_2O$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
P	2333(1)	1686(1)	4933(1)
O(1)	611(2)	1324(1)	5476(1)
O(2)	4302(3)	1686(2)	5585(2)
O(3)	7763(3)	2850(2)	6149(2)
C(1)	2472(3)	789(2)	3688(2)
N	576(2)	297(1)	3121(1)
C(2)	−944(3)	1207(2)	2761(2)
C(3)	−2818(4)	637(3)	2213(2)
C(4)	−2487(5)	−112(3)	1222(2)
C(5)	−905(5)	−1012(2)	1592(2)
C(6)	963(4)	−443(2)	2132(2)

Table 2 Selected distances (Å) and angles (°) for $HL^1 \cdot H_2O$ with e.s.d.s in parentheses

P–H(p)	1.34(3)	N–C(2)	1.500(3)
P–O(1)	1.488(1)	N–C(6)	1.513(4)
P–O(2)	1.469(2)	O(4)–H(w1)	0.82(3)
P–C(1)	1.828(2)	O(4)–H(w2)	0.81(3)
N–C(1)	1.497(3)	N–H(n)	0.96(3)
H(p)–P–O(1)	104(1)	C(1)–N–C(2)	113.5(2)
H(p)–P–O(2)	113(1)	C(1)–N–C(6)	109.4(2)
H(p)–P–C(1)	103(1)	C(2)–N–C(6)	110.9(2)
O(1)–P–O(2)	119.9(1)	H(w1)–O(3)–H(w2)	112(3)
O(1)–P–C(1)	109.5(1)	H(n)–N–C(1)	110(1)
O(2)–P–C(1)	106.7(1)	H(n)–N–C(2)	105(1)
P–C(1)–N	116.3(1)	N(n)–N–C(6)	107(1)
Hydrogen bonds*			
O(2)···O(3)	2.735(6)	O(2)···H(w2)	1.95(4)
O(1)···O(3^{I})	2.828(7)	O(1)···H(w1^{I})	2.05(3)
N···O(1^{II})	2.710(6)	H(n)···O(1^{II})	1.77(2)
O(2)···H(w2)–O(3)	163(2)	N–H(n)···O(3^{II})	167(2)
O(1)···H(w1^{I})–O(3^{I})	158(2)	H(w1^{I})···O(1)···H(n)	99(3)

* Symmetry codes: I $x-1, y, z$; II $-x, -y, 1-z$.

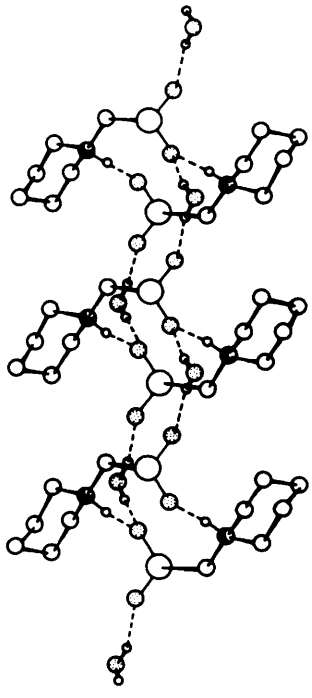


Fig. 2 View of $HL^1 \cdot H_2O$ showing hydrogen-bonding interaction within the chains

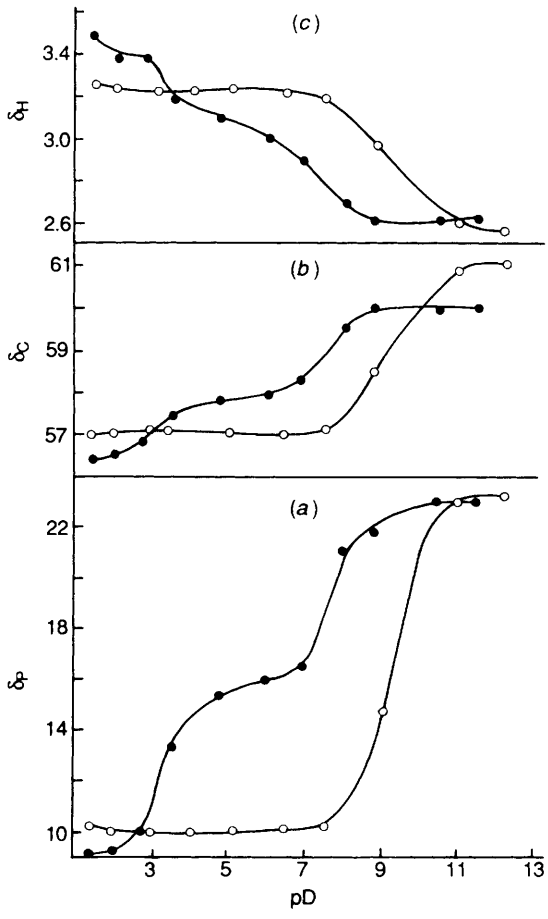


Fig. 3 Variation with pD of (*a*) δ_P, (*b*) δ_C and (*c*) δ_H of the methylenephosphinic group for solutions of HL^1 (○) and H_2L^2 (●) in D_2O

water molecules. The network of hydrogen bonds is shown in Fig. 2. Each H_2O molecule participates in two hydrogen bonds as a 'donor of proton'. The oxygen atom O(1) from the phosphinic group is an acceptor of two protons [one from the protonated nitrogen atom and the other from a water molecule; O(1)···O(3^{I}) 2.828(7) Å, O(1)···H(w1^{I})–O(3^{I}) 158(2) °]; atom O(2) accepts only one proton from a H_2O molecule [O(2)···O(3) 2.735(6) Å, O(2)···H(w2)–O(3) 163(2)°].

NMR Spectra.—Plots *vs.* pD of δ_H and δ_C for NCH_2P and δ_P for the two acids are shown in Fig. 3 and parameters are listed in Table 3. It is clear from NMR titrations of aminomethylenephosphonic[13] and phosphinic acids[1,14] that in the ^1H and ^{13}C plots each deprotonation step causes a change in the same direction. For ^{31}P, deprotonation of the phosphonic(-inic) group shifts δ_P to lower values, while deprotonation of the last nitrogen causes a much more pronounced deshielding of the phosphorus nucleus. From this point of view, the distinct 'breaks' in the plots of chemical shift (Fig. 3) correspond to deprotonation of the N atoms. Therefore, the favoured zwitterion forms for the two free acids would be expected in solution. X-Ray crystal structure determinations[11,12] have shown that the solid acids of this type exist in this form and our plots also indicate its presence in solution. Two 'breaks' in the case of H_2L^2 indicate independence of the N atoms of the piperazine ring and demonstrate stability of the chair conformation of this ring. The *gauche* conformation would be indicated by only a simple 'break', in analogy with ethylenediamine-*N*,*N*,*N*′,*N*′-tetrakis[methyl(phenyl)phosphinic acid].[1] On the other hand, the estimated pK_A values and the shape of the curves indicate that the phosphinic groups are completely deprotonated within the studied region. The ^{31}P

Table 3 NMR parameters of the protonated species of HL^1 and H_2L^2 (J in Hz)

	pD	δ_P	δ_C ($^1J_{PC}$)	δ_H ($^2J_{PH}$)	δ(Hp) ($^1J_{PH}$)	$\delta(H^2)$	$\delta(C^2)$ ($^3J_{PC}$)
HL^1 *	1.43	10.30	57.02 (70.7)	3.201 (10.7)	7.225 (548.3)	a 3.07 e 3.62	56.68 —
$(L^1)^-$ *	10.96	23.09	60.86 (102.0)	2.596 (11.3)	7.141 (511.8)	2.645	56.76 (8.7)
H_2L^2	1.41	9.11	56.48 (81.9)	3.462 (10.3)	7.311 (555.5)	3.918	51.70 (4.6)
$(HL^2)^-$	4.79	15.52	57.79 (92.6)	3.002 (10.7)	7.160 (530.6)	3.271	53.43 (6.4)
$(L^2)^{2-}$	10.49	22.37	60.03 (102.3)	2.590 (11.4)	7.067 (514.4)	2.719	54.85 (8.9)

* For HL^1, δ 23.87 (C^3) and 21.82 (C^4); for $(L^1)^-$, δ 25.88 (C^3) and 24.03 (C^4).

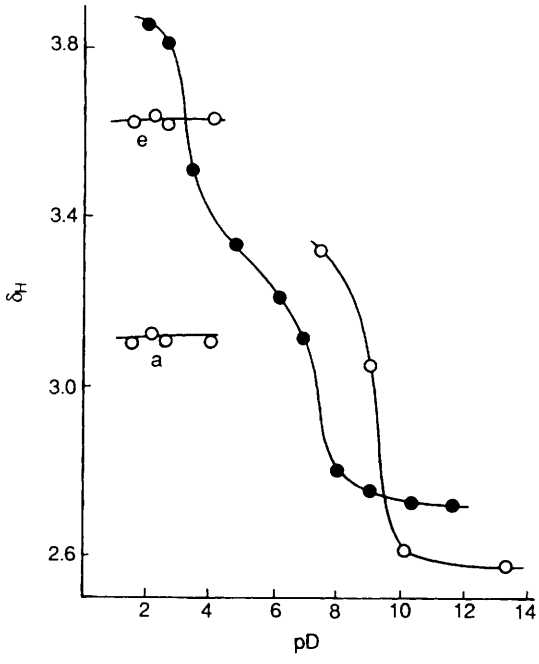


Fig. 4 Variation with pD of δ_H of HL^1 ring C^2 protons (○) (e = equatorial, a = axial) and H_2L^2 ring protons (●)

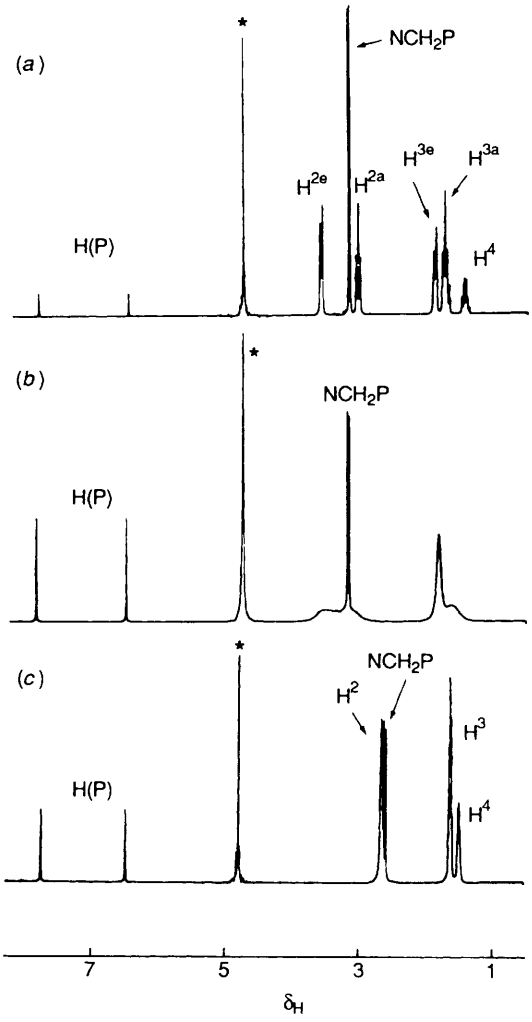


Fig. 5 The ^1H NMR spectra of HL^1 at pD 1.43 (*a*), 6.47 (*b*) and 10.96 (*c*) (e = equatorial, a = axial; * = water protons)

NMR spectra of the two acids indicate the P–H $\rightleftharpoons$ P–D exchange in the region pD 1–3 and in the strongly alkaline region, pD $\approx$ 13, as observed by Pokrovskaya[15] and Fluck[16] and co-workers for analogous compounds.

The dependence on pD of δ_H for the H atoms of the piperazine ring is similar to that for the NCH_2P group. In contrast to H_2L^2, the δ_H dependence of the piperidine ring shows an influence of the protonated nitrogen atom on the conformation. Fig. 4 depicts the δ_H dependence on pD for the hydrogen atoms bonded to C(2) of the piperidine ring and Fig. 5 the ^1H NMR spectra at pD 1.4, 6.5 and 11.0. The behaviour seems to be analogous to that in the case of N-methylpiperidine.[17] In the acidic region, when the N atom is protonated, the HL^1 configuration would probably be the same as that in the solid state, with an equatorial $CH_2PHO_2^-$ (see Fig. 1) and inversion of the ring would not occur or be slow on the NMR time-scale. The NMR peaks due to both the axial and equatorial hydrogen atoms are pronounced. The values of ^2J(H–H) ($\approx$ 13 Hz) and ^3J(H–H) ($H^{2a}H^{3a}$, $\approx$12; $H^{2a}H^{3e}$, $\approx$2.8 Hz) for the hydrogen atoms bonded to C(2) are close to those for *N*-methylpiperidine hydrochloride.[17] The values for all H atoms confirm the $X_2X'_2A_2A'_2BB'$ pattern proposed by Booth and Little[17] on the basis of the ^1H NMR spectra of the C(2) hydrogen atoms of *N*-methylpiperidine. In accordance with the distribution diagrams obtained from the potentiometric measurement (see Fig. 6), 10–15% of the molecules are deprotonated in a region pH 4.5–7. In this region, the resonances for the piperidine hydrogen atoms are very broad. In the alkaline region, when a large fraction of the nitrogen atoms is deprotonated, ^1H NMR spectra of the piperidine ring correspond to a $(X_2)_2(A_2)_2B_2$ pattern (see Fig. 5).

All these facts indicate that inversion of the piperidine ring is hindered in the presence of the protonated HL^1 form. As with *N*-methylpiperidine, deprotonation makes rapid inversion at N possible and consequently leads to an inversion of the ring. In

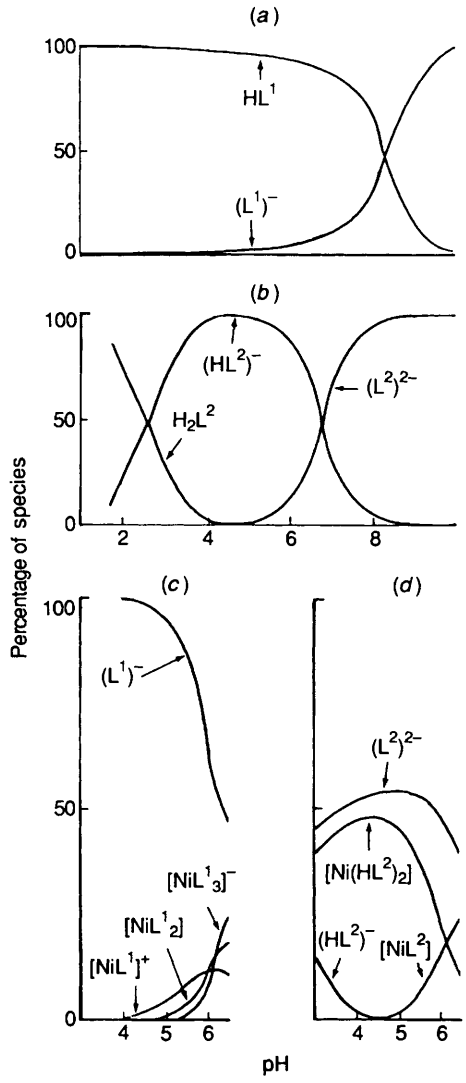


Fig. 6 Distribution diagrams of free ligands HL^1 (*a*) and H_2L^2 (*b*) (c_L = 0.005 mol dm^{-3}) and their solutions with nickel(II) (*c*) and (*d*) (c_{Ni} = 0.005, c_L = 0.015 mol dm^{-3})

contrast to Eliel *et al.*,[18] we did not observe another isomer of the piperidine ring in our ^{13}C NMR spectra of HL^1.

Potentiometric Titration.—The values determined for pK_A and log β for complexes of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Mg^{2+} and Ca^{2+} are listed in Table 4 and the distribution diagrams of the two acids with examples for the metal complexes are given in Fig. 6.

The potentiometric data are consistent with the NMR titration curves. Only the pK_A values for the protonated nitrogen atoms could be determined. The values for phosphinic groups may be much lower than 1 because they could not be calculated, even from titration curves starting at a pH of about 1.3. The potentiometric pK_A values agree with the NMR estimates. A comparison of basicity of the nitrogen atoms with the values for *N*-piperidineacetic acid (HL^3)[19] (10.25), piperazine-1,4-diacetic acid (H_2L^4)[19] (4.46, 8.70) and the phosphonic analogue (H_4L^5)[20] (4.61, 5.72, 8.02, 10.47) indicates basicity increasing in the order HL^1 < HL^3 or H_2L^2 < H_2L^4 < H_4L^5. The same order was observed for ethylenediaminetetraacetic acid (H_4edta) analogues[1] and recently for R′CH(NH_2)PO(R″)-OH (R′,R″ = H, alkyl or aryl).[4b] In accord with Parker and co-workers,[10] we attempted to calculate higher values of pK_A (about 13) from titration to pH ≈ 13, using a special calibration of a glass electrode in the alkaline region,[21] but without success. Therefore, we assume that the observed increasing basicity of

Table 4 Dissociation (protonation) constants of HL^1 and H_2L^2 and stability constants of their complexes at 25 °C and I = 0.1 mol dm^{-3}; $\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r$

Cation	p	q	r	HL^1	p	q	r	H_2L^2
	0	1	1	8.41(1)	0	1	1	6.719(3)
H^+ [a]					0	2	1	2.622(7) [9.341]
Mg^{2+}	1	0	1	3.46(2)	1	0	1	(0.6)[b]
Ca^{2+}	1	0	1	3.05(2)				—
	1	0	1	4.231(8)	1	0	1	1.72(4)
Co^{2+}	1	0	2	8.30(2)	1	2	2	15.9(4)[b]
	1	0	3	11.87(1)				
	1	0	1	4.45(1)	1	0	1	3.16(2)
Ni^{2+}	1	0	2	8.65(3)	1	2	2	17.98(3)
	1	0	3	12.84(3)				
	1	0	1	4.91(2)[b]	1	0	1	3.18(3)
Cu^{2+}					1	2	2	17.79(6)
	1	0	1	4.46(2)[b]	1	0	1	1.49(5)
Zn^{2+}					1	1	1	8.31(4)
	1	0	1	3.95(2)[b]	1	0	1	2.16(3)
Cd^{2+}					1	1	1	8.66(4)
Pb^{2+}				precipitate	1	0	1	1.39(8)

[a] pK_A calculated by the program ESAB2M (log β_2 in square brackets). [b] The values were not refined exactly, due to low content of complexes.

the nitrogen atoms in the order aminomethylene-phosphinic < -carboxylic < -phosphonic would also be found for other analogues of amino acids. A comparison of H_2L^2 with ethylenediamine-*N*,*N*′-bis(methylphosphinic) acid[2] (H_2L^6) indicates an analogous increase in the acidity of the nitrogen atoms to that of similar carboxylic acids.[19] The pK_A decrease from 8.08 and 4.98 (H_2L^6) to 6.718 and 2.621 (H_2L^2) is probably caused by repulsion of the positive charges on the protonated nitrogen atoms in the rigid piperazine ring. The chair conformation and rigidity probably prevent a further stabilization of the proton by interaction with another nitrogen atom or oxygen of the phosphinic group in the same molecule.

On the basis of the X-ray structural data for complexes with the $NCH_2P(R)O_2^-$ system we found several possibilities for co-ordination of the tested ligands. The simplest form, monodentate co-ordination of the phosphinic group *via* the protonated N atom, was observed in $[MnCl_2\{NH_3^+CH_2P(CH_3)O_2^-\}(H_2O)_2]$.[5] The analogous complexes $[ZnCl_2\{NH_3^+CH_2P(CH_3)O_2^-\}]$[8] and $[CuCl_2\{NH_3^+CH_2P(CH_3)O_2^-\}(H_2O)]_2$,[6] form inifinite polymeric chains Zn–O–P–O–Zn– or a dimeric form with two –O–P–O– bridges connecting two copper atoms. A co-ordinated amino group was found[7] only in $[Cu_2Cl_2\{NH_2CH_2P(CH_3)O_2\}_2]$ but phosphinic groups again formed O–P–O bridges connecting two copper atoms.

The compound HL^1 forms complexes in different ratios of 1:1 to 1:3 in the region pH 4–7 only with Co^{2+} and Ni^{2+}. For Cu^{2+}, Zn^{2+} and Cd^{2+}, log β values of ≈4 were found only at a ratio of 1:1. However, the concentration of these species $[ML^1]^+$ was only 3–4% and therefore the values were not refined exactly. Relatively higher values for Mg^{2+} and Ca^{2+} could be explained by the hard character of HL^1. The calculated log β values as well as the reversibility of the titration procedures indicate the chelating form of the complexes but only in a narrow pH region. Precipitates were formed at pH ≈ 7 for all metals studied and for Pb^{2+} at pH ≈ 1. We assume polymeric forms of the complexes precipitate, and this was confirmed by orientative analysis for the system with Cu^{2+}. The results correspond with the solid-state X-ray investigation mentioned above and the ability of the phosphinic moiety to form polymeric chains. In comparison with log β values for the Cu–$CH_3CH(NH_2)$-PO(H)OH system,[4b] HL^1 forms a polymeric chain more easily

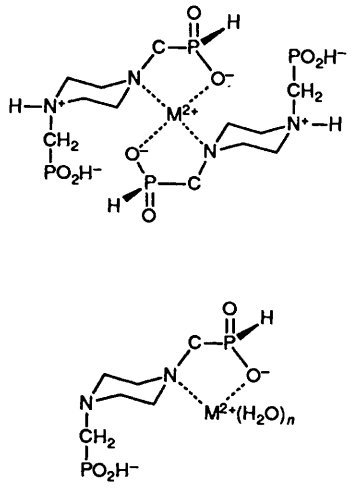


Fig. 7 Possible structures of $[M(HL^2)_2]$ and $[ML^2(H_2O)_n]$ complexes (M = Co^{II}, Ni^{II} or Cu^{II}) in solution

probably due to the lower co-ordination ability of the N atom in the piperidine ring.

In spite of the presence of two nitrogen atoms and two phosphinic groups, H_2L^2 forms significantly weaker complexes than those of HL^1 in the pH region 4–7 (Table 3) and the carboxylic analogue H_2L^4.[19] It also forms a precipitate at pH ≈ 7. However, in contrast to HL^1, formation of protonated complexes was observed, probably due to the rigidity of the piperazine ring. Therefore, the inversion of piperazine ring to the *gauche* conformation and subsequent co-ordination of both N atoms to the metal cannot be assumed. In our opinion, as in Fig. 7, only one side of H_2L^2 is co-ordinated to the metal as a chelate through nitrogen and oxygen of the phosphinic group in 1:1 or 1:2 complexes and the opposite side may be protonated. The complexes formed with Mg^{2+} and Ca^{2+} were too weak for quantitative treatment.

Experimental

Preparation of $HL^1 \cdot H_2O$, $H_2L^2 \cdot 2H_2O$ *and Chemicals.*—The compounds $HL^1 \cdot H_2O$ and $H_2L^2 \cdot 2H_2O$ were prepared by the Mannich reaction according to Maier.[22] Recrystallization of $HL \cdot H_2O$ was carried out by dissolving the crude product in ethanol and passing diethyl ether vapour through the ethanolic solution. Crystals of $HL^1 \cdot H_2O$ for the X-ray study were obtained in the same way; $H_2L^2 \cdot 2H_2O$ was recrystallized by introducing ethanol vapour into an aqueous solution. $HL^1 \cdot H_2O$, m.p. 170 °C (lit.,[22] 146–147 °C) (Found: C, 39.7; H, 9.05; N, 7.80; P, 16.8. Calc. for $C_6H_{17}NO_3P$: C, 39.7; H, 8.90; N, 7.70; P, 17.1%). $H_2L^2 \cdot 2H_2O$, m.p. 269–271 °C (lit.,[22] 238–242 C) (Found: C, 25.9; H, 7.40; N, 10.0; P, 22.1. Calc. for $C_6H_{20}N_2O_6P_2$: C, 25.9; H, 6.85; N, 10.0; P, 22.6%).

The stock solutions of the individual metal cations were acidified solutions of the perchlorates, prepared by reaction of the metal oxides or carbonates (p.a.) with a slight excess of p.a. perchloric acid (Merck). The metal content in the solution was determined by titration with an edta solution and excess of perchloric acid was determined by pH metric acid–base titration using a DTS 833 titrator with a recommended program.

Crystallographic Studies.—Crystal data for $HL^1 \cdot H_2O$. $C_6H_{17}NO_3P$, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), a = 6.884(2), b = 11.485(2), c = 11.994(2) Å, β = 97.87(2)°, U = 939.4(6) Å^3 (by least-squares refinement of diffractometer angles for 15 automatically centred reflections in the range 20 17–30°), λ = 1.5718 Å, D_m = 1.27(1) g cm^{-3}, Z = 4, D_c = 1.281 g cm^{-3}, $F(000)$ = 392, colourless crystals, dimensions 0.6 × 0.5 × 0.5 mm, μ(Cu-Kα) = 24.9 cm^{-1}.

Syntex $P2_1$ diffractometer, ω–2θ scan mode, graphite-monochromated Cu-Kα radiation, 1795 reflections measured (h −15 to 0, k −15 to 0, l −20 to 20; $2\theta_{max}$ = 122°), 1356 of them 'observed' with $I > 1.96\sigma(I)$; no absorption correction. The structure was solved by direct methods (SHELXS 86),[23] thermal parameters (anisotropic for non-hydrogen, isotropic for hydrogen atoms); the scale factor and secondary isotropic extinction coefficient were refined simultaneously by full-matrix least squares (SHELX 76).[24] Scattering factors for neutral atoms were taken from ref. 25. The refinement converged at R = 0.042, R' = 0.085 with the largest residual peak of 0.32 e Å^{-3}. The weighting scheme was $w = 1/(\sigma^2 F_o + 0.0009F_o^2)$, isotropic type I extinction correction with Lorentz distribution,[26] g = 6.5(6) × 10^{-6}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

NMR Spectra.—The NMR spectra were measured using a Varian XL-200 instrument at 24 °C: ^{1}H at 200.057 MHz with sodium 4,4-dimethyl-4-silapentane-1-sulfonate as the internal standard, ^{31}P at 80.53 MHz with 85% H_3PO_4 as the external standard and ^{13}C NMR at 50.308 MHz with sodium 4,4-dimethyl-4-silapentane-1-sulfonate as the external standard. The ^{13}C-{^{1}H} and ^{31}P-{^{1}H} spectra were measured using wide-band proton decoupling. Samples were prepared by dissolving the acids in 10% NaOD solution in D_2O. The pD value was adjusted by addition of 25% $DClO_4$ solution in D_2O or NaOD in D_2O. It was calculated from the formula pD = pH + 0.40, where pH is the value read on the pH meter calibrated according to the manufacturers instructions. The measured solutions had a concentration of 10% (w/v).

Potentiometric Titrations.—Potentiometric measurements were carried out using a PHM 84 pH-meter, ABU 80 autoburette and a GK 2401B combination electrode (Radiometer) in a glass vessel (150 cm^3) thermostatted at 25 ± 0.1 °C at an ionic strength of I($NaClO_4$) = 0.1 mol dm^{-3}. An inert atmosphere was ensured by constant passage of argon saturated with the solvent vapour. The initial solution volume was 50 cm^3 and the HL^1 or H_2L^2 concentration was 0.005 mol dm^{-3}. In the determination of the stability constants of the transition-metal complexes the metal concentration was 0.005 mol dm^{-3} and the metal:ligand ratio was 1:1, 1:2 or 1:3. After calibration using two buffers, precision calibration was carried out by a titration of 0.01 mol dm^{-3} $HClO_4$ with 0.1 mol dm^{-3} NaOH with the pH meter yielding E values. The value E_0 in the equation $E = E_0 + S(-\log[H])$ was calculated for each series of measurements by the ESAB2M program with the theoretical value S = 59.16. The values of pK_A and log β were calculated using the same program and MINIQUAD 82 using the calibration E_0 values.

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