Phosphonate Complexes. Part 6.[1] Influence of Steric Effects, Solvation, and Chelation on Stability

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The interaction of some phosphonic acids $RPO(OH)_2$, chosen to introduce different controlling factors ($R = Bu^t$, cyclo-C_6H_{11}, Ph, n-$C_{10}H_{21}$, Me_2NCMe_2, CH_2SEt, $CH_2CH_2CO_2^-$), with Ca^{II} and Cu^{II} has been investigated by potentiometry at 25 °C, $I = 0.1$ mol dm^{-3} ($K[NO_3]$). The selection of the species and the refinement of the stability constants illustrates the applicability of a new version of the program MUCOMP. Examination of linear free-energy plots indicates that factors other than polar effects are of significance, *i.e.* chelate formation with the potentially bidentate ligands and particularly solvation effects which preferentially stabilize the complexes of α-branched-chain phosphonates. Other features (steric hindrance, predominance of some microscopic forms) are discussed.

A NEW version of the multiparametric refinement program MUCOMP for complex formation studies from potentiometric data has been reported in the preceding paper. The applicability of this program is illustrated, in the present work, by the determination of stability constants of complexes of Cu^{II} and Ca^{II} with particular phosphonates RPO_3^{2-}, for which one might expect a stabilization owing to the presence (i) of bulky alkyl groups ($R = Bu^t$, cyclo-C_6H_{11}, Ph, n-$C_{10}H_{21}$, Me_2NCMe_2) or (ii) of a donor atom in the alkyl chain ($R = CH_2SEt$, Me_2NCMe_2, $CH_2CH_2CO_2^-$). The results were expected to complete our information on the co-ordination ability of phosphonates. The preliminary examination of linear free-energy plots,[2] for Cu^{II} complexes of amino-alkylphosphonic acids $H_3\overset{+}{N}CR^1R^2[CH_2]_nPO_3H^-$, reveals indeed appreciable positive deviations when (i) R^1 or R^2 are alkyl chains and $n = 0$ [3] or (ii) $R^1 = H$, $R^2 = CO_2H$, $n = 1$,[4] indicating that factors other than inductive effects are of significance. Furthermore, the crystal structure determination of (hydroxymethylphosphonato)copper(II) dihydrate [5] has showed the occurrence of bonding between copper atoms and un-ionized hydroxy-groups. This confirms that the presence of a donor atom in the alkyl side-chain enhances the stability by chelate formation.[6]

EXPERIMENTAL

Materials.—t-Butylphosphonic acid was prepared from the corresponding phosphonyl dichloride. The latter was readily obtained by the method outlined by Kinnear and Perren [7] and purified by vacuum sublimation. Its hydrolysis, which is much more difficult than for the lower members,[6,8] was achieved by prolonged reflux with an excess of water. Further recrystallization in water gave needle-shaped crystals (Found: C, 34.65; H, 7.8; P, 22.35. Calc. for $C_4H_{11}O_3P$: C, 34.8; H, 7.95; P, 22.45%).

The hydrolysis of cyclohexylphosphonyl dichloride (Alfa Products), carried out as above, yielded cyclohexylphosphonic acid which was purified by recrystallization from water (Found: C, 44.0; H, 7.9; P, 18.8. Calc. for $C_6H_{13}O_3P$: C, 43.9; H, 8.0; P, 18.85%).

The Arbuzov reaction, applied to 1-bromodecane (Alfa Products) and triethyl phosphite (Fluka, purum) with removal of the resulting ethyl bromide,[9] yielded diethyl n-decylphosphonate. The hydrolysis with an excess of hydrochloric acid (6 mol dm^{-3}) under reflux gave a precipitate of n-decylphosphonic acid which was purified by further recrystallization in ligroin.

Diethyl (1-dimethylamino-1-methylethyl)phosphonate was prepared, according to the method of Fields,[10] from diethyl phosphite (Fluka, purum), dimethylamine, and acetone. The crude ester, which can be hydrolyzed to the acid only by drastic methods, was refluxed for 4 h with a 48% solution of hydrobromic acid. After evaporation, the residue was purified by an elution chromatographic method on Amberlite IR 120 (H^+ form) resin. The solution of the acid, which is eluted with water after the strongly acidic species, was concentrated and gave the free acid $Me_2H\overset{+}{N}CMe_2PO_3H^-$ by addition of an excess of ethanol (Found: C, 34.0; H, 7.8; N, 8.5; P, 18.55. Calc. for $C_5H_{14}NO_3P$: C, 35.95; H, 8.45; N, 8.4; P, 18.55)%.

Diethyl (ethylthiomethyl)phosphonate (Alfa Products) was hydrolyzed to the corresponding acid by refluxing for 10

TABLE 1

Survey of the titrations

Acid	$C_A{}^0$/ mol dm^{-3}	$C_A{}^0/C_M{}^0$ for Cu^{II}	$C_A{}^0/C_M{}^0$ for Ca^{II}	pH at the beginning of Cu^{II} precipitation ($C_A{}^0/C_M{}^0 = 1.5$)
$PhPO(OH)_2$	2×10^{-3}	1; 1.5	1	6.3
$(n\text{-}C_{10}H_{21})PO(OH)_2$*	10^{-3}			
$(cyclo\text{-}C_6H_{11})PO(OH)_2$	$(1 \text{ or } 2) \times 10^{-3}$	1; 1.5; 3	1	5.7
$Bu^tPO(OH)_2$	2×10^{-3}	1; 1.5	1	6.2
$Me_2NCMe_2PO(OH)_2$	2×10^{-3}	1.5; 2; 2.5; 3		6.6
	10^{-2}		1	
$EtSCH_2PO(OH)_2$	2×10^{-3}	1; 1.5	1	6.5
$HO_2CCH_2CH_2PO(OH)_2$	10^{-3}	1; 1.5	1	6.15

* With preliminary addition of 0.95 mol of KOH per mol of acid.

h with hydrochloric acid (6 mol dm^{-3}). Since no solvent suitable for recrystallization could be found, the acid was neutralized to pH 5 with potassium carbonate and the monopotassium salt was recrystallized from water–ethanol mixtures. Solutions of the acid were generated by elution of the salt on a strongly acidic resin on H^+ form (Amberlite IR 120). Phenylphosphonic acid (Aldrich) was recrystallized from water; 3-phosphonopropionic acid (Alfa Products) was used without further purification.

The purity of these compounds, checked by pH titrations, was in all cases higher than 99.5%.

TABLE 2

'Best' results of multiparametric refinements applied to the system Cu^{II}–(ethylthiomethyl)phosphonate[a]

	$H_i^0 = 0$	$H_i^0 \neq 0$
(a) Common parameters		
$\log \beta_{0-10}$	−13.847(9)	−13.882(8)
$\log \beta_{011}$	7.061(7)	7.055(4)
$\log \beta_{021}$	8.81(3)	8.82(2)
$\log \beta_{101}$	4.15(2)	4.150(7)
$\log \beta_{102}$	7.3(2)	7.28(8)
$\log \beta_{1-11}$	−3.1(2)	−3.09(9)
$\log \beta_{2-20}$	−10.72	−10.72
(b) Particular parameters		
Titration 1: ligand alone (30 experimental points)		
C_{A1}^0	$1.917(2) \times 10^{-3}$	$1.884(6) \times 10^{-3}$
C_{M1}^0	10^{-12}	10^{-12}
H_{i1}^0	0	$3.3(7) \times 10^{-5}$
C_{i1}^0	0	0
H_{x1}^0	−0.1925	−0.1925
C_{x1}^0	$0.8(2) \times 10^{-3}$	$2.6(4) \times 10^{-3}$
α_1	3×10^{-4}	3×10^{-4}
E_{01}	−0.055	−0.055
P_1	1.00	1.00
Titration 2: ligand + Cu^{II} (34 experimental points)		
C_{A2}^0	$1.908(2) \times 10^{-3}$	$1.875(1) \times 10^{-3}$
C_{M2}^0	1.182×10^{-3}	1.182×10^{-3}
H_{i2}^0	0	3.3×10^{-5}
C_{i2}^0	0	0
H_{x2}^0	−0.1925	−0.1925
C_{x2}^0	0.8×10^{-3}	2.6×10^{-3}
α_2	3×10^{-4}	3×10^{-4}
E_{02}	−0.055(3)	−0.054(1)
P_2	1.00	1.00
s[b]	1.93	0.85

[a] Values in parentheses are the estimated errors (3σ) in the last significant figure of the refined parameters [b] W_n Calculated from equation (8) of ref. 1 with $\sigma_{0v} = 2.10^{-4}$, $\sigma_{0E} = 10^{-3}$, and $k = 5$. Concentrations are expressed in mol dm^{-3}.

The preparation of standardized hydrochloric acid, and the preparation and analysis of calcium(II) and copper(II) nitrates have been described in ref. 6. Potassium hydroxide solutions (0.1—0.2 mol dm^{-3}) were obtained by dilution of a concentrated solution previously prepared from washed pellets of potash. Unfortunately, these titrants were contaminated with carbonate whose concentration represents 1—2% of the OH^- concentration. Moreover, we think that the term 'carbonate-free' is used improperly because it rarely corresponds to reality.

All the solutions were made with boiled distilled water.

Apparatus and Titration Procedure.—The automated titration system, including a micrometer syringe Gilmont (2.5 cm^3) adapted to the automatic burette,[11] described in ref. 12, was used. All studies were carried out at 25.00 ±0.05 °C the ionic strength being brought to a mean value of 0.1 mol dm^{-3} by potassium nitrate addition.[6] A stream of purified and presaturated nitrogen was passed over the solution. After each titrant delivery, the pH reading was stored when the pH drift was less than 0.001 pH unit min^{-1} or after a preset waiting time of 6 min. This maximum time is always reached for experimental points where (i) HCO_3^- is the predominant form of the carbonate species and (ii) the local slope $\Delta pH/\Delta v$ high, *i.e.* near an equivalent point. This mode of data collection ensures a satisfactory reproducibility in the parts of the titration where the carbonate equilibria are slowly displaced.

The pH meter and electrodes (Schott, type N 65 combined electrode) were calibrated against both potassium phthalate [pH(S) = 4.008] and borax [pH(S) = 9.180] solutions prepared according to NBS specifications.

The zero shift of the electrodes (E_0), the ionic product of water ($K_w = \beta_{0-10}$), the characteristic figures of the strong base ($H_x^0 < 0$, total concentration of the alkali-metal ion; C_x^0 = total concentration of the carbonate), and the carbon dioxide evolution coefficient α were periodically checked, using the MUPROT program[13] applied to titrations of standardized hydrochloric acid (2×10^{-3} mol dm^{-3}) with potassium hydroxide. These titrations were performed in a closed system ($\alpha = 0$, C_x^0 obtained) or under nitrogen (C_x^0 fixed, α obtained). In all cases, the liquid junction coefficients J_a and J_b were found to be negligible. The glass electrode is then calibrated as a concentration probe [equation (5) of ref. 1] and consequently the equilibrium constants are expressed as concentration quotients.

Protonation constants for the free ligands and formation constants for the metal complexes were determined from titrations in the absence or in the presence of Ca^{II} and Cu^{II}, respectively. Table 1 gives a summary of these titrations. At least two titrations were carried out for each system. In the case of (1-dimethylamino-1-methylethyl)phosphonic acid, more concentrated solutions were used to reach a higher pH value, where the last dissociation was noticeable. Owing to the low solubility of n-decylphosphonic acid, the titrations were started with a partially neutralized acid. Under these conditions, Ca^{II} and Cu^{II} species were sparingly soluble and thus prevented any complex formation study.

Usually, 40—50 experimental data points were collected during a titration, except when precipitation took place: the pH meter readings then showed a continuous downward drift and the titration was ended. This occurred for Cu^{II}, beyond the equivalent volume, corresponding to: $RPO_3H^- \longrightarrow RPO_3^{2-} + H^+$, and led to a basic phosphonate.[6]

Particular Determinations.—The first acidity constants ($K_1^H = [H^+][HA^-]/[H_2A]$) of phenyl- and ethylthiomethylphosphonic acids are greater than 10^{-2} mol dm^{-3} and the conventional methods fail to give accurate values of the constants. Therefore, a particular potentiometric method,[14] suitable for moderately strong acids, was applied.

CALCULATIONS

The recorded experimental data, *i.e.* added volumes and pH, were processed using the improved version of the MUCOMP program.[1] The main features of the MUCOMP approach being the weighting procedure and the parameterization of the possible systematic errors; the calculations were conducted as follows.

Weighting Factors.—The values of σ_{0v}, σ_{0E}, and k which enter in the weighting factor W_n [equation (8) of ref. 1] were chosen from the following considerations. The resolutions at the syringe (10^{-4} cm^3) and of the pH meter (0.001 pH unit) gave *a priori* estimates of the uncertainties σ_{0v} and σ_{0E}: in that case, and if we neglect the CO_2 evolution ($k = 0$), the weights become important in the steeper parts of the titration curve [Figure 1(*a*)]. However, it is well known that a pH drift $\partial E/\partial t$ occurs when the local slope $\partial E/\partial v$ is high. This leads to an additional constant term [13] in W_n, if $\partial E/\partial t$ is proportional to $\partial E/\partial v$, which can be included in σ_{0v}. As expected, the increase of σ_{0v} moderates W_n in the parts of the curve where potential drifts are perceptible [Figure 1(*b*)]. We have previously introduced and selected a third term to reduce the W_n values corresponding to data where the CO_2 departure disturbs chiefly the equilibria: it can be seen from Figure 1 that the weights decrease in a pH range where HCO_3^- is predominant. Finally, it was postulated that acceptable values of σ_{0v}, σ_{0E}, and k should lead to a variance of residuals, $s^2 = S$/degrees of freedom, close to unity, in absence of any systematic error. In most of our refinements, this external normalisation gave a set close to $\sigma_{0v} = 2 \times 10^{-4}$, $\sigma_{0E} = 0.001$, and $k = 5$. These values were assumed to be constant for all the titrations.

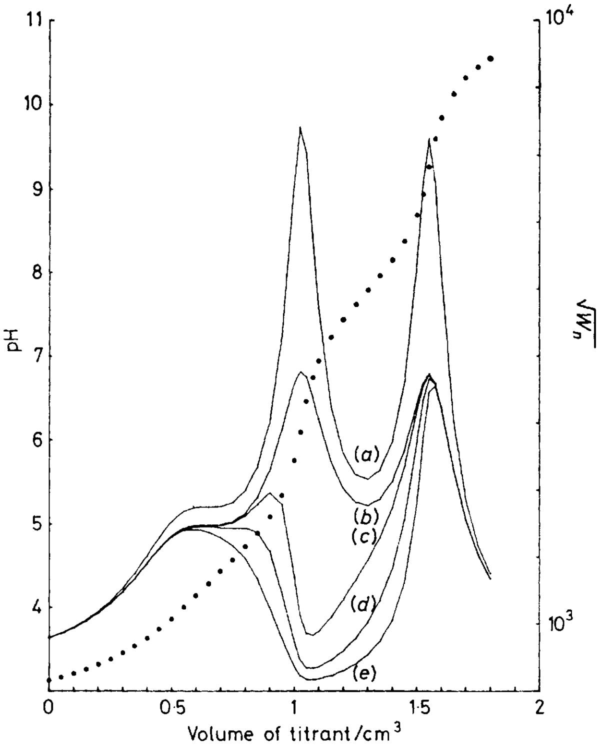

FIGURE 1 Titration curve for phosphonopropionic acid (●) and plots of $\sqrt{W_n} = f(V_n)$. The weighting factors were calculated from equation (8) of ref. 1 with $\sigma_{0E} = 0.001$ and (*a*) $\sigma_{0v} = 10^{-4}$, $k = 0$; (*b*) $\sigma_{0v} = 2 \times 10^{-4}$, $k = 0$ (*c*) $\sigma_{0v} = 2 \times 10^{-4}$, $k = 2$; (*d*) $\sigma_{0v} = 2 \times 10^{-4}$, $k = 5$; and (*e*) $\sigma_{0v} = 2 \times 10^{-4}$, $k = 10$

Refinement of the Parameters.—The sensible rule is to refine those parameters that have a significant influence on the data. In the course of the refinements, if parameters become strongly correlated or if too large standard deviations appear, then additional parameters must be fixed, if known, or neglected. For example, it was not possible to adjust simultaneously the evolution coefficient α and the added concentration of carbonate C_x^0 which are highly correlated. Therefore C_x^0 was obtained from a titration performed in a closed system for which carbonate conservation is effective. Another titration performed under nitrogen gave a value for α, C_x^0 being fixed. In the further calculations, one of these parameters was kept constant (α in most cases). The total concentration of the metal ion can also be refined but the corresponding standard deviation is high and it is better to introduce the value obtained by chemical analysis.

In the most favourable case, the data corresponding to titrations of the free ligand and of metal ion–ligand mixtures were processed at the same time with the MUCOMP program. The ligand experiments can be handled by this program, just by introducing a negligible value for C_M^0 (here $C_M^0 = 10^{-12}$ mol dm^{-3}). The fixed values were usually the hydrolysis constants of the metal ions [$\log \beta_{1-10} = -12.9$ for $Ca(OH)^+$ and $\log \beta_{2-20} = -10.7$ for $Cu_2(OH)_2^{2+}$],[8] H_x^0, C_M^0, C_i^0, $\alpha = (3—4) \times 10^{-4}$, $P = 1.00$, and $J_a = J_b = 0$. Furthermore, for the titrations involving the free ligand, E_0, which is strongly correlated with the first acidity constant, was fixed at the value obtained from neutralization of a strong acid (observed mean value of $E_0 = -0.055$). The refined parameters were (i) the stability constants, including the protonation constants and K_w; (ii) the total concentrations of the ligand C_A^0, of added carbonate C_x^0, and, in certain cases, of a strongly acidic impurity H_i^0; and (iii) the zero shift E_0 for the complex formation titrations which may slightly change owing to the small differences of ionic strength. Initial estimates for stability constants were obtained from our previous works on phosphonate complexes. In the case of Cu^{II} complex formation, it was not always realistic to adjust C_x^0 or H_i^0 which were then maintained at a mean value obtained from titrations of the free ligand.

It is always possible to adopt the habitual two-level strategy. The protonation constants, C_A^0, C_x^0, H_i^0, E_0, P, C_i, and α are first refined with MUPROT [13] from titration data of the ligand. The stability constants are then adjusted by means of the MUCOMP program with some of the previous parameters having fixed values, *e.g.* protonation constants.

The importance of some systematic errors to the goodness of the fit, and therefore to the selection of the best model, is illustrated by Figure 2, for the system Cu^{II} and $EtSCH_2PO_3^{2-}$ (A^{2-}). The calculations were made from the data of two different pH titrations, the first corresponding to the ligand alone and the second to the ligand in the presence of the metal ion. Several hypotheses about the stoicheiometry of the species present [CuA, CuA_2^{2-}; CuA, $Cu(OH)A^-$; CuA, CuA_2^{2-}, $Cu(OH)A^-$] have been confronted with various sources of systematic errors. When systematic errors were assumed to be absent from the second titration, *i.e.* the C_{A2}^0, H_{i2}^0,

C_{x2}^0, and E_{02} values were supposed to be identical to those obtained from the first titration, the fits were always poor ($5.0 < s < 7.2$) and none of the tested models was significantly better than the other. The refinement of the total ligand concentration relative to the second titration gave, in all cases, significantly lower variances of weighted residuals (s^2), which were improved again by considering an initial proton excess H_i^0. However, s^2 approximates to unity, *i.e.* the expected variance of the measurements in absence of any systematic error, only for the model CuA, CuA_2^{2-}, and $Cu(OH)A^-$ which can then be unambiguously retained. The resultant ' best ' values of the parameters are listed in Table 2 alongside those obtained with a neglected initial proton excess. The stability constants agree in general within the uncertainty of 3σ, indicating a weak dependence upon this kind of systematic error. However, the standard deviations are noticeably reduced when H_i^0 is refined. This proton excess ($H_i^0 = 3.3 \times 10^{-5}$ mol dm^{-3}) is not surprising since it can be explained by the particular obtention of the solution of $EtSCH_2PO_3H_2$ which was generated by elution of the corresponding monopotassium salt on a strongly acidic ion exchanger. This salt presumably contained small amounts of potassium chloride which then gave hydrochloric acid. Furthermore, we can note that the concentration of added carbonate ($C_x^0 = 2.6 \times 10^{-3}$ mol dm^{-3}) agrees very well with the expected value ($C_x^0 = 2.9 \times 10^{-3}$ mol dm^{-3}). The values of log β_{021} are in good concordance with that obtained from a particular potentiometric method (Table 3). It is finally reassuring to observe only very small changes in E_0. The repeated standardizations of the electrodes and the choice of a mean value of the ionic strength, which includes the contribution of the metal ion, ensure in most cases reproducible values of E_0.

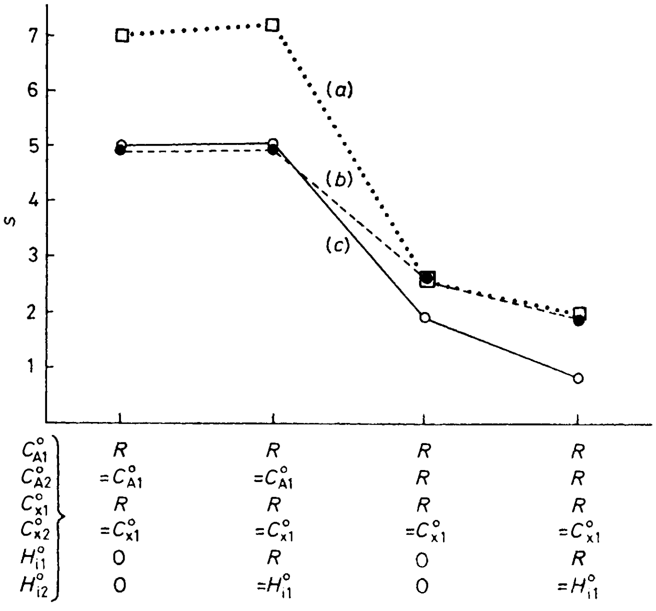

FIGURE 2 Plots of $s = (S/\text{degrees of freedom})^{\frac{1}{2}}$, for various chemical models [(*a*) CuA, $Cu(OH)A^-$; (*b*) CuA, CuA_2^{2-}; (*c*) CuA, $Cu(OH)A^-$, CuA_2^{2-}; with $A^{2-} = EtSCH_2PO_3^{2-}$] against different sets of refined systematic errors. *R* Refers to a refined parameter and subscripts 1 and 2 to the titrations 1 and 2. The other refined and fixed parameters were those of Table 2

TABLE 3

Protonation constants for the ligands (A^{2-}) and stability constants for the metal complexes $M_qH_jA_p$, at 25 °C and $I = 0.1$ mol dm^{-3} ($K[NO_3]$); σ denotes the standard deviation

Ligand	*q*	*j*	*p*	Species	log β_{qjp}(3σ)
$PhPO_3^{2-}$	0	1	1	HA^-	7.021(0.005)
	0	2	1	H_2A	8.70(0.03)
	1	0	1	CaA	1.43(0.15)
	1	0	1	CuA	3.18(0.04)
	1	−1	1	$Cu(OH)A^-$	−3.65(0.05)
$(n\text{-}C_{10}H_{21})PO_3^{2-}$	0	1	1	HA^-	7.965(0.01)
$(cyclo\text{-}C_6H_{11})PO_3^{2-}$	0	1	1	HA^-	8.173(0.006)
	0	2	1	H_2A	10.66(0.02)
	1	0	1	CaA	1.65(0.07)
	1	0	1	CuA	3.97(0.08)
$Bu^tPO_3^{2-}$	0	1	1	HA^-	8.44(0.01)
	0	2	1	H_2A	11.07(0.03)
	1	0	1	CaA	1.69(0.08)
	1	0	1	CuA	4.14(0.03)
$Me_2NCMe_2PO_3^{2-}$	0	1	1	HA^-	12.22(0.05)
	0	2	1	H_2A	17.958(0.045)
	1	1	1	$Ca(HA)^+$	13.25(0.08)
	1	0	1	CaA	1.2(0.2)
	1	1	1	$Cu(HA)^+$	14.70(0.05)
	1	0	1	CuA	8.27(0.04)
	1	−1	1	$Cu(OH)A^-$	0.91(0.1)
	1	2	2	$Cu(HA)_2$	28.92(0.3)
$EtSCH_2PO_3^{2-}$	0	1	1	HA^-	7.055(0.004)
	0	0	1	H_2A	8.80(0.03)
	1	0	1	CaA	1.70(0.10)
	1	0	1	CuA	4.150(0.007)
	1	−1	1	$Cu(OH)A^-$	−3.09(0.09)
	1	0	2	CuA_2^{2-}	7.28(0.08)
$^-O_2CCH_2CH_2PO_3^{2-}$ (A^{3-})	0	1	1	HA^{2-}	7.708(0.005)
	0	2	1	H_2A^-	12.231(0.01)
	0	3	1	H_3A	14.24(0.03)
	1	0	1	CaA^-	1.72(0.1)
	1	1	1	Cu(HA)	9.93(0.1)
	1	0	1	CuA^-	4.28(0.07)

RESULTS AND DISCUSSION

The refined protonation and stability constants are given in Table 3. The second protonation constants of phenyl- and ethylthiomethyl-phosphonic acids were calculated from $\log \beta_{021} = \log \beta_{011} + pK_1^H$, pK_1^H being determined as outlined in the Experimental section. The comparison of the acid dissociation constants of 3-phosphonopropionic acid, $HO_2CCH_2CH_2PO_3H_2$ ($pK_1^H = 2.01$, $pK_2^H = 4.523$, and $pK_3^H = 7.708$), calculated from Table 3 values, with those of carboxylic [15] and phosphonic acids [6] indicates a stepwise dissociation of $-PO_3H_2$, $-CO_2H$, and $-PO_3H^-$. All the protonation constants are easily rationalized by the inductive and the steric effects of the substituents. The second controlling factor is particularly perceptible for α-branched-chain acids. For example, the log protonation constants of some representative phosphonic acids RPO_3H^- and the corresponding polar substituent constants [16] σ_R are (i) R = $ClCH_2$, log $\beta_{011} = 6.169$,[6] $\sigma_R = 1.05$, (ii) R = Me, log $\beta_{011} = 7.547$,[6] $\sigma_R = 0.00$, and (iii) R = Bu^t, log $\beta_{011} = 8.440$, $\sigma_R = -0.30$. We can consider that polar effects alone are of importance in the ionization of the first two acids and it follows that $\Delta(\log \beta_{011})/\Delta\sigma_R = -1.31$. Thus the acid weakening between methyl- and t-butyl-phosphonic acids is much more important [$\Delta(\log \beta_{011})/\Delta\sigma_R = -2.98$] than predicted from the previous variation. The explanation of this additional acid-weakening must lie in the inhibition of the solvation by the alkyl side chains, which will preferentially reduce the stability of RPO_3^{2-} since this anion is more highly solvated than RPO_3H^-. The same phenomenon is observed for $R = n\text{-}C_{10}H_{21}$, cyclo-$C_6H_{11}$, and $Me_2H\overset{+}{N}CMe_2$.

TABLE 4

Differences between experimental and expected values of log β_{101}

Ligand	$\Delta(\log \beta_{101})$ for Ca^{II} complexes	$\Delta(\log \beta_{101})$ for Cu^{II} complexes
$PhPO_3^{2-}$	−0.02	−0.10
$(\text{cyclo-}C_6H_{11})PO_3^{2-}$	0.10	0.19
$Bu^tPO_3^{2-}$	0.11	0.25
$EtSCH_2PO_3^{2-}$	0.25	0.86
$^-O_2CCH_2CH_2PO_3^{2-}$	0.21	0.70

As expected, more important gains in stability are encountered when additional donor atoms (sulphur or carboxyl oxygen) are introduced, the complexes being stabilized by chelate formation. A comparison of the donor abilities of the sulphur and of the carboxylate is not easy because the gain in chelation energy will be different, since the chelates have different ring sizes (five members for $EtSCH_2PO_3^{2-}$ and seven for $^-O_2CCH_2CH_2PO_3^{2-}$). If we consider that this kind of stabilization decreases rapidly with the ring-size enlargement, we can suggest that there is a stronger interaction between the oxygen donor atom of the carboxylate group and copper. However, in $[Cu(O_3PCH_2SEt)]$ which exhibits a noticeable stabilization [$\Delta(\log \beta_{101}) = 0.86$], the sulphur atom might be bound in the equatorial square plane about the central Cu^{II} rather than in an axial position, which was observed for the hydroxyl group in (hydroxymethylphosphonato)copper(II) [$\Delta(\log \beta_{101}) = 0.28$, from ref. 6].

To explain the more complicated behaviour of the system Cu^{II}–$Me_2NCMe_2PO_3^{2-}$–H^+ we have reported in Table 5 some typical values relating to parent compounds.

TABLE 5

Acidity constants K_j^H and stability constants of some (aminoalkylphosphonato)copper(II) complexes

H_2A		$pK_2^H = \log(\beta_{021}/\beta_{011})$	$pK_3^H = \log \beta_{011}$	$\log \beta_{101}$	$\log K_{Cu(HA)}^{Cu} = \log(\beta_{111}/\beta_{011})$	Ref.
$H_3\overset{+}{N}CH_2PO_3H^-$	(1)	5.39	10.05	8.12	2.51	3
$H_3\overset{+}{N}CMe_2PO_3H^-$	(2)	5.805	10.31	9.13	3.37	3
$MeH_2\overset{+}{N}CH_2PO_3H^-$	(3)	5.310	10.912	8.29	2.41	3
$Me_2H\overset{+}{N}CH_2PO_3H^-$	(4)	5.184	11.063	7.99	2.30	3
$Me_2H\overset{+}{N}CMe_2PO_3H^-$	(5)	5.738	12.22	8.27	2.48	This work

The formed complexes are quite analogous to those of parent ligands. Hydroxo-complexes were undetectable for cyclohexylphosphonate, t-butylphosphonate, and 3-phosphonatoproprionate for which a precipitation of copper phosphonate occurs rapidly; for the same reason, the usual CuA_2^{2-} complex [3] was not detected in the case of the aminophosphonate. In a previous study,[6] linear correlations were obtained between stability constants of substituted alkylphosphonate complexes ($\log \beta_{101}$) and the corresponding protonation constants ($\log \beta_{011}$): (*a*) $\log \beta_{101} = 0.80 + 0.092 (\log \beta_{011})$ for Ca^{II}; (*b*) $\log \beta_{101} = 0.23 + 0.434 (\log \beta_{011})$ for Cu^{II}.

We have reported in Table 4 the differences between the experimental stability constants of Table 3 and the values predicted from these linear relationships.

The positive deviations observed when alkyl side-chains are introduced in the vicinity of the $-PO_3^{2-}$ function, which are particularly significant for Cu^{II} complexes, can also be attributed to a steric inhibition of solvation. The formation of the neutral complex MA, which is less solvated than the anion A^{2-}, is then favoured. These considerations can also be applied to α-aminoalkylphosphonates which exhibit comparable properties (see some examples in Table 5). The different behaviour of phenylphosphonate complexes is most probably the result of a stabilization of the anion by resonance.

As pointed out before, the combination of polar and solvation effects is responsible for the changes in the acidities of the $-PO_3H^-$ (pK_2^H) and of the protonated amine (pK_3^H) groups. However, while the changes in pK_2^H are nearly identical when two methyl groups are introduced as alkyl side chains [$\Delta pK_2^H = 0.415$ between acids (1) and (2), and $\Delta pK_2^H = 0.554$ between (4) and (5), see Table 5] the increase of stability on the corresponding complexes $Cu(HA)^+$ are discordant [$\Delta(\log K_{Cu(HA)}^{Cu}) = 0.86$ and 0.18 respectively]. The previous hypothesis concerning the stabilization of branched-chain phosphonate complexes seems to fail when the amine nitrogen comports alkyl chains. This discrepancy can yet be explained if we consider that the 'macroscopic' complex $Cu(HA)^+$ corresponds in fact to two different 'microscopic' species, *i.e.* (I) $[CuNR_2CR_2PO_3H]^+$ and (II) $[R_2HNCR_2PO_3Cu]^+$, where R = H or CH_3. This hypothesis is supported by the examination of the distribution curves of the different 'macroscopic' species: the domain of $Cu(HA)^+$ existence is almost entirely included in that of CuA, for which nitrogen is unambiguously bound to copper. It ensues that the microscopic form (I) is less likely when alkyl groups are attached to amino-nitrogen, the macroscopic constant being then correlatively attenuated. Conversely, in the case of the acid H_2A, one branch of the microscopic ionization scheme ($R_2H\overset{+}{N}CR_2PO_3H^- \rightleftharpoons R_2H\overset{+}{N}CR_2PO_3^{2-} + H^+$)

is much more important than the other ($R_2\overset{+}{H}NCH_2PO_3H^- \rightleftharpoons R_2NCH_2PO_3H^- + H^+$) since the domains of dissociation of these two protonated groups are quite different, *i.e.* the protonated site corresponding to pK_2^H is well located and the properties of alkylphosphonic acids are directly transposable.

The deprotonation of $Cu(HA)^+$ results in a chelate CuA involving the amino-moiety and one oxygen of the phosphonate group. It can be seen from Table 5 that the stability of the chelate is governed by (i) the basicity of the amino-group, (ii) its steric hindrance, and (iii) solvation effects. The influence of the first two controlling factors is evident; in series (1),(2) and (4),(5) the trend of pK_3^H is the same as that of log β_{101} and when the degree of substitution increases on nitrogen a reversed trend is noted between log β_{101} and pK_3^H [series (1), (3), (4)]. As before, the introduction of methyl groups in the α position produces different effects depending on whether the amino-moiety is substituted or not [Δ(log β_{101}) = 1.01 between complexes of (2) and (1); Δ(log β_{101}) = 0.28 between (5) and (4)]. Solvation effects are still responsible for that deviation. According to the large amount of work done on the base strengths of amines [17,18] it appears that hydration of an alkylammonium ion is directly proportional to the number of hydrogens attached to nitrogen; the different species corresponding to tertiary amino-moieties are poorly hydrated and thus less sensitive to stabilization by solvation.

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