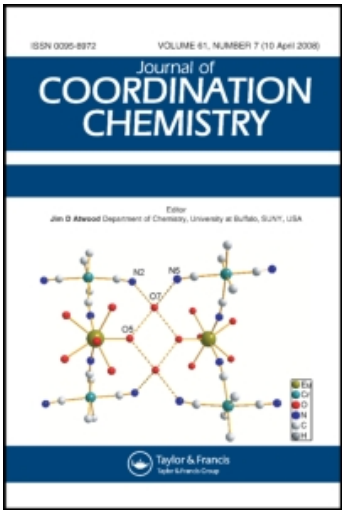

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Equilibrium Studies of the Protonation of 8-Quinolyl Phosphate, 1-Naphthyl Phosphate and 8-Quinolyl Methyl Phosphate and their Complexation with Copper(II), Zinc(II), Nickel(II), Cobalt(II) and Manganese(II) Ions in Aqueous Solution

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EQUILIBRIUM STUDIES OF THE PROTONATION OF 8-QUINOLYL PHOSPHATE, 1-NAPHTHYL PHOSPHATE AND 8-QUINOLYL METHYL PHOSPHATE AND THEIR COMPLEXATION WITH COPPER(II), ZINC(II), NICKEL(II), COBALT(II) AND MANGANESE(II) IONS IN AQUEOUS SOLUTION

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8-Quinolyl dihydrogen phosphate, 1-naphthyl dihydrogen phosphate and monosodium 8-quinolyl methyl phosphate were synthesized. Extensive potentiometric investigations were made of the equilibrium complexation of the three anions, 8-quinolyl phosphate (**1**), 1-naphthyl phosphate (**2**), and 8-quinolyl methyl phosphate (**3**) with hydrogen, copper(II), zinc(II), nickel(II) and cobalt(II) ions in aqueous solution at 25°C and I = 150 mmol dm^{-3} (Na^+) [Cl^-]. Equilibria between **1** and manganese(II) ions were also studied. The protonation equilibrium results augmented by NMR measurements were interpreted as indicating that the first proton to be bound by **1** becomes shared between the quinolinium nitrogen and a phosphate oxygen. The metal complexation results indicated the formation of the mononuclear binary complex, ML, in each case. In addition, copper(II), zinc(II) and nickel(II) ions formed the hydroxo complex, MLH_{-1}, with **1**, **2**, and **3**. Zinc(II) also formed the protonated complex, ZnLH with **1**. Also with L = **1**, $CuLH_{-1}$, $ZnLH_{-1}$ and ZnLH were found to be very significant complexes whereas $NiLH_{-1}$ was found only in relatively low concentrations.

Keywords: 8-Quinolyl phosphate, 1-naphthyl phosphate, complexes, stability constants

INTRODUCTION

Hydrolytic reactions of phosphorus esters are widespread in biological systems and these are generally mediated by divalent metal ions.[1–3] In an endeavour to shed light on the detailed mechanisms of these reactions and the role of the metal ions, much work has been done on model systems.[3–9] The latter include the investigations by Murakami and Sunamoto of the influence of various metal ions on the hydrolysis of 8-quinolyl phosphate.[1,3] These authors conclude that two successive interactions between the metal and the substrate are involved in the catalyzed reaction. The

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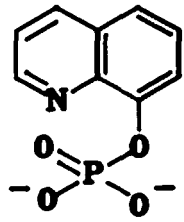
interaction consists of chelation of the metal between the heterocyclic nitrogen atom and one of the non-ester phosphate oxygens. In the subsequent step, an intramolecular rearrangement takes place to form a chelate between the heterocyclic nitrogen and the ester oxygen atom. In their potentiometric studies of the initial interaction with copper(II) and nickel(II) ions Murakami and Sunamoto (*loc. cit.*) conclude that appreciable concentrations of $CuHL^+$ and CuL are formed whereas complexation by nickel(II) ions is slight. (The ligand species, L^{2-}, is illustrated in **1**).

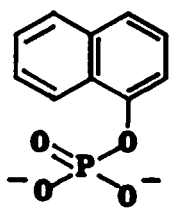


1

Murakami and Sunamoto's potentiometric titrations were, however, limited to concentrations of 2.0×10^{-3} mol dm^{-3} and $1.0–2.0 \times 10^{-3}$ mol dm^{-3} for the ligand and metal ion, respectively.

In the present paper, we report the results of a more extensive potentiometric study and NMR investigations aimed at exploring the initial interaction between metal ions and 8-quinolyl phosphate, in greater detail. We have considered not only **1** but also the related ligands, 1-naphthyl phosphate (**2**) and 8-quinolyl methyl phosphate (**3**) and their interactions with copper(II), nickel(II), zinc(II), cobalt(II) and manganese(II) ions. Ligands **2** and **3** differ from **1** in the absence of one potential donor centre (the nitrogen atom and one of the non-ester oxygen atoms, respectively) and thus it seemed interesting to compare their behaviour with that of **1**.

The temperature at which the experiments have been conducted, namely 25°C, is substantially lower than those at which the hydrolysis of these organophosphorus compounds proceeds significantly.



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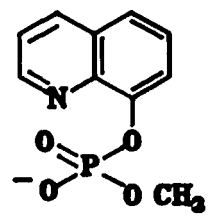

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EXPERIMENTAL

Chemicals

Reagents used for synthesis of the ligands consisted of charcoal (BDH), diphosphorus pentoxide (Merck), potassium hydroxide, (Laboratory and Scientific Equipment) and sodium metal (BDH), which were used as supplied. In addition, acetone,

acetonitrile, potassium chloride, sodium iodide (Laboratory and Scientific Equipment), dioxane, phosphoryl chloride, phosphorus trichloride, sulphuryl chloride (Merck), benzene ether, methylethylketone (N. and T. Laboratory Supplies) and methanol (UnivAR) were purified by drying and/or distillation. 8-Hydroxyquinoline (Merck) was purified by recrystallization from ethanol:water (6:3). 1-Naphthol (Hopkin and Williams) was purified by recrystallization from distilled water in the presence of activated charcoal.

Chemicals used for the potentiometric and NMR experiments were as follows. Sodium hydroxide solutions (0.01 mol dm^{-3}) were freshly prepared at frequent intervals by dilution of the contents of Merck ampoules, under nitrogen, and standardized against potassium hydrogen phthalate (Merck). Hydrochloric acid solutions (0.01 mol dm^{-3}) were also prepared by the use of Merck ampoules and standardized against the sodium hydroxide solutions. Carbonate-free copper(II), nickel(II), cobalt(II) and manganese(II) chloride solutions were prepared from Merck G.R. salts. Zinc(II) chloride solutions were prepared by dissolving accurately weighed zinc granules in concentrated hyrochloric acid and subsequent dilution in a volumetric flask. All of the solutions were prepared using carbonate-free, boiled out, glass distilled water and were made up to a total chloride concentration of 0.150 mol dm^{-3} using solid sodium chloride (BDH "Aristar"). The metal chloride solutions were analyzed by titration against Na_2H_2edta* (BDH) and for mineral acid by Gran titration.[10] Nitrogen (Afrox), obtained from a high purity cylinder, was passed through concentrated potassium hydroxide, Fieser's solution,[11] an empty wash bottle and through ionic background solution thermostatted at 25°C. After it had passed through the titration vessel, the nitrogen was released to the atmosphere *via* a trap containing the ionic background solution, to prevent back diffusion of oxygen and carbon dioxide. Water-d_2 (Goss) and chloroform-*d* (Merck) were used as supplied.

^{1}H NMR spectra were recorded in deuterated water (with the sodium salt of 3[trimethylsilyl]-propanesulfonic acid as internal reference) or in deuterated chloroform (with tetramethylsilane as internal reference) on a Varian EM-360A spectrometer. Mass spectra were measured on a VG Analytical Micromass 16F spectrometer operating at 70eV with an ion source temperature of 200°C. Melting points (uncorrected) were determined on a Fisher-Johns m.p. apparatus. Aluminium-backed silica gel plates (Merck, Kieselgel $60F_{254}$ Art. 5554) were used for thin layer chromatography. Analyses for C, H, N were performed on a Heraeus Universal combustion analyser by Mr. W.R.T. Hemsted of the Organic Chemistry Department, University of Cape Town.

Synthesis of the Ligands

The syntheses were carried out with the strict exclusion of moisture.

1-Naphthyl dihydrogen phosphate

1-Naphthyl phosphorodichloridate[12] was prepared by refluxing 1-naphthol (0.1072 mol) and phosphoryl chloride (0.6432 mol) for 8 hours in the presence of a catalytic amount of potassium chloride (0.0001 mol). The solution was cooled and then distilled, the fraction boiling at 164°C (0.1 mmHg) being collected as the pure,

* edta = ethylenediaminetetraacetate

desired product (79%). The conversion of 1-naphthyl phosphorochloridate to 1-naphthyl dihydrogen phosphate[13] was effected by placing the former as a 2–3 mm thick layer in a flat dish over aqueous potassium hydroxide, in a partially evacuated desiccator for 3 days. The white solid so formed was dried over silica gel and diphosphorus pentoxide (to remove traces of water) and potassium hydroxide pellets (to remove traces of hydrochloric acid). Yield: 96%; m.p.: 159–161°C (lit.[13] m.p. 155–157°C); ^{1}H NMR (D_2O): δ 8.61 (1H, dd, $J_{H,H}$[ortho] 8Hz, $J_{H,H}$[meta] 2Hz) proton *ortho* to naphthyl oxygen, δ 7.38 – 7.92 (6H,m) remaining aromatic protons; MS: m/e 224(M^+); m/e 144 (base, M–HPO_3); Anal. calc. for $C_{10}H_7O_4P$: C: 53.56;H: 4.05% Found: C: 53.60; H: 4.05%.

8-Quinolyl dihydrogen phosphate

8-Hydroxyquinoline (0.0499 mol) was dissolved in pyridine (40 cm^3) and added dropwise, over a period of 2 hours, to a solution of phosphoryl chloride (0.2490 mol) in dioxane (40 cm^3), with stirring and cooling in ice. Immediate formation of a white precipitate of pyridinium chloride was observed. Once the addition was completed stirring was continued for 30 minutes and then the resulting mixture was allowed to stand overnight at room temperature. The pyridinium salt was collected by gravity filtration and the excess phosphoryl chloride, pyridine and dioxane were removed from the filtrate, *in vacuo*, at 50°C, to leave a thick yellow liquid. To this was added pyridine (100 cm^3), dioxane (100 cm^3) and then, with good stirring and dropwise addition, water (2.5 cm^3). The reaction mixture was stirred for a further 30 minutes before being left to stand overnight. The solvents were removed *in vacuo* and the desired 8-quinolyl dihydrogen phosphate was separated, as white crystals, from the pyridinium chloride by repeated recrystallization from water:acetonitrile (1:1). Yield: 40%; m.p. 170–174°C (lit.[14] m.p. 218–220°C); ^{1}H NMR (D_2O): δ 9.20–9.37 (2H,m) protons at positions 2 and 7 in the 8-hydroxyquinoline system, δ 8.08–8.33 (4H,m) remaining aromatic protons; MS: no M^+, m/e 145 (base, 8-hydroxyquinoline); Anal. calc. for $C_9H_8O_4NP$: C: 48.01; H: 3.59; N: 6.22%. Found: C: 47.95; H: 3.65; N: 6.25%.

8-Quinolyl methyl phosphate (monosodium salt)

The sodium salt of 8-hydroxyquinoline was prepared by dissolving 8-hydroxyquinoline in a minimum volume of ethanol and adding, with stirring, an equimolar amount of sodium hydroxide dissolved in a minimum volume of water. A thick yellow precipitate of the desired salt formed immediately; it was collected by suction filtration and dried at 120°C to give an olive green powder of constant mass and almost quantitative yield.

Dimethyl phosphorochloridate[15] was prepared by the dropwise addition, over a period of 1 hour, of a solution of phosphorus trichloride (0.5040 mol) in benzene (44 cm^3), to a stirred solution of methanol (1.5041 mol) in benzene (150 cm^3), while maintaining a reaction temperature of between 5 and 10°C. Once this addition was completed the temperature was lowered further to 0°C as sulphuryl chloride (0.5001 mol) was slowly added, with stirring. This mixture was then left to stand overnight at room temperature to allow the gaseous products to escape. Benzene was removed *in vacuo* and the crude dimethyl phosphorochloridate was purified by distillation at the water pump (yield: 80%).

8-Quinolyl dimethyl phosphate was synthesized by dissolving dimethyl phosphorochloridate (0.0845 mol) in ether (200 cm^3) and adding, portionwise, the sodium salt

8-hydroxyquinoline (0.0845 mol) with stirring and cooling in ice such that the mperature of the reacting solution remained below 15°C. As the reaction pro-eded, a light brown precipitate of sodium chloride was observed to form. After dition of the salt was completed, the mixture was allowed to stand overnight in der to ensure complete reaction. The precipitate of sodium chloride was removed gravity filtration and centrifugation. The ether was evaporated from the filtrate *in cuo* to yield pale yellow crystals of 8-quinolyldimethyl phosphate. Yield: 74%; m.p. –68°C; ^{1}H NMR ($CDCl_3$): δ 9.1 (1H, dd $J_{H,H}$[ortho]4Hz; $J_{H,H}$[meta] 1Hz) aromatic oton *ortho* to quinolyl nitrogen, δ 8.23 (1H, dd, $J_{H,H}$[ortho]9Hz; $J_{H,H}$[meta] 1Hz) omatic proton *ortho* to hydroxyl function of 8-hydroxyquinoline system, δ 7.38–7.90 (4H,m) remaining aromatic protons, δ 4.05 (6H, dd, $^3J_{H,P}$12Hz) methyl otons; MS; m/e 253 (M^+); m/e 158 (base, M^+–$MeOPO_2H$); Anal. calc. for $_{11}H_{12}NO_4P$: C: 52.17; H: 4.79; N: 5.53%. Found: C: 52.20; H: 4.80; N: 5.45%.

8-Quinolyl methyl phosphate (sodium salt) was obtained by the monodemethyl-ion[16,17] of 8-quinolyl dimethyl phosphate. 8-Quinolyl dimethyl phosphate .0040 mol) and sodium iodide (0.0040 mol) were dissolved in acetone (100 cm^3) and ated under reflux, using an air condenser, for four hours. After cooling, the etone was removed *in vacuo* to leave a yellow powdery solid which was found, by I NMR, to be a mixture of the desired sodium salt and an acetone dimer. 8-uinolyl methyl phosphate was isolated by dissolving the crude product in aceto-:rile (40 cm^3) and pouring this solution into ether (200 cm^3). A fine yellow precipi-:e fell out of solution; it was collected by centrifugation and identified as pure quinolylmethyl phosphate (mono-sodium salt). Yield: 85%; m.p. undetermined as e salt is very hygroscopic; ^{1}H NMR (D_2O): δ 8.70 (1H, dd, $J_{H,H}$[ortho]4Hz, $J_{H,H}$ eta]1Hz proton *ortho* to quinolyl nitrogen, δ 8.08 (1H, dd, $J_{H,H}$[ortho]10Hz, $J_{H,H}$ eta]1Hz proton *ortho* to the hydroxyl function in 8-hydroxyquinoline system, 7.27–7.70 (4H,m) remaining aromatic protons, δ 3.77 (3H, d, $^3J_{H,P}$11Hz) methyl otons; MS: no M^+; m/e 145 (base, 8-hydroxyquinoline); Anal. calc. for $C_{10}H_9$-$O_4PNa.H_2O$: C: 43.02; H: 3.98; N: 5.02%. Found: C: 42.55; H: 3.85; N: 4.8%.

Owing to the hygroscopic nature of sodium 8-quinolyl methyl phosphate solutions r the potentiometric titrations were prepared freshly and assayed by means of rations against standardized hydrochloric acid or sodium hydroxide.

otentiometric Measurements

uilibrium constants for the protonation of the ligands and the complexation of the ands by the metal ions were determined by potentiometric titrations in a Metrohm 876-20 titration vessel maintained at 25.0 ± 0.1°C. The electrodes were two etrohm EA109 glass electrodes used alternately and a Metrohm EA404 calomel erence electrode containing a saturated sodium chloride solution (BDH "Aristar") electrolyte. Solutions containing ligand and metal chloride (zero concentration for e protonation titrations) were titrated with either the hydrochloric acid–chloride lution or the sodium hydroxide–chloride solution. Alternatively, some of the mplexation titrations were carried out by titrating the ligand solution with either drochloric acid–chloride or sodium hydroxide–chloride solution to a predeter-ned approximate pH. Subsequently metal chloride solution (0.05 mol dm^{-3}) was rated into the solution. The titrant solutions were added from a Metrohm Dosimat 35 piston burette controlled by a Metrohm Titroprocessor E636, which also easured and recorded the emf of the cell together with the corresponding volume of rant added.

The alternative complexation titration procedure had the advantage that a considerably greater range of extent of complexation was attainable without interference from precipitate formation, than by the more usual procedure of adding acid or alkali to a solution containing ligand and metal.

The electrodes were calibrated at the pertinent ionic strength by means of strong acid–strong base titrations.

Computations

The protonation constants were determined approximately by applying Bjerrum's method to the formation curves generated by the ZBAR task of ESTA.[18] The complexation titration data were processed initially by the BETA task and subsequently by the ZBAR and QBAR tasks of ESTA, in order to facilitate the selection of species. Refinement of the formation constants (β_{pqr}*) was performed by running the complexation titration data on the ESTA optimization module with weighted least-squares objective function based on emf residuals (OBJE) and with point to point ionic strength correlations (D–HC block).

With a view to reducing the effects of systematic errors in the data, certain of the refinement runs were carried out with simultaneous optimization of the formation constants and other titration parameters such as concentration of the components and electrode intercept.[19] The formation constant values obtained were checked against those obtained by MINIQUAD.[20] Good agreement was found in all cases.

The validity of the finally chosen chemical models and sets of "best" formation constants were checked by graphical comparision of the observed formation and deprotonation curves with the corresponding ESTA-generated calculated curves. In all cases, the appropriate metal hydrolysis reactions[21] were incorporated into the individual chemical models applied to the various metal-ligand systems.

NMR Titrations and Investigation of Stacking

^{31}P spectra of the solutions were recorded on a Varian VXR200 spectrometer. NMR "titrations" were performed with a view to identifying the sites of protonation on 8-quinolyl phosphate. A series of solutions, (0.008 mol dm^{-3}), each at a specific pH within the range 1 to 7, was prepared. Each solution was introduced to a NMR tube and into this was inserted a capillary tube containing deuterium oxide and trimethyl phosphate which were used for the purposes of providing a lock and internal standard, respectively.

Further NMR experiments were carried out in order to establish whether intermolecular stacking interactions would affect the ^{31}P spectrum of 8-quinolyl phosphate. In these, spectra were recorded for a series of solutions covering the concentration range 0.002 to 0.016 mol dm^{-3}. The pH of each solution was adjusted to 6.2.

RESULTS AND DISCUSSION

Protonations

Titrations of each ligand, at a concentration of *ca* 0.005 mol dm^{-3}, were performed up to a pH of *ca* 7.5. No attempt was made to determine the third protonation

* β_{pqr} refers to the general complex $M_pL_qH_r$, where M = metal ion, L = ligand and H = proton. When r is negative, this refers to the removal of protons to water molecules or to a hydroxide ligand added.

TABLE I

Logarithms of formation constants (β_{pqr}) determined at 25°C and I = 0.15 mol dm^{-3} (Na^+)[Cl^-]; d = standard deviation in lgβ; n_o = number of experimental observations; n_t = number of titrations; R = Hamilton factor.

Ligand	Cation	p q r	$\lg\beta_{pqr}$	d	n_t	n_o	pH range	R
1	H^+	0 1 1	6.33_3	0.001	4	265	2.0–9.0	0.0008
		0 1 2	10.46_2	0.002				
	Cu^{2+}	1 1 0	5.11_4	0.005	10	318	2.2–6.0	0.0103
		1 1–1	-0.91_0	0.012				
	Zn^{2+}	1 1 0	4.87_0	0.012	7	263	2.2–6.5	0.0215
		1 1–1	-1.69_7	0.036				
		1 1 1	9.69_5	0.014				
	Ni^{2+}	1 1 0	2.34_5	0.010	6	269	3.0–7.5	0.0204
		1 1–1	-5.46_9	0.027				
	Co^{2+}	1 1 0	1.78_1	0.024	6	294	2.3–7.0	0.0111
	Mn^{2+}	1 1 0	1.90_9	0.015	7	245	3.5–8.0	0.0133
2	H^+	0 1 1	5.74_0	0.005	4	301	2.0–8.0	0.0020
	Cu^{2+}	1 1 0	2.63_5	0.006	6	207	2.0–6.0	0.0026
		1 1–1	-3.84_0	0.021				
	Zn^{2+}	1 1 0	2.01_4	0.011	14	400	2.0–6.0	0.0049
		1 1–1	-4.73_0	0.025				
	Ni^{2+}	1 1 0	1.56_8	0.006	7	84	4.0–6.0	0.0244
	Co^{2+}	1 1 0	1.68_1	0.002	5	139	4.5–6.0	0.0104
	Mn^{2+}	Not studied						
3	H^+	0 1 1	4.72_5	0.001	6	246	2.0–8.0	0.0017
	Cu^{2+}	1 1 0	2.52_3	0.004	8	277	2.2–6.2	0.0048
		1 1–1	-4.06_2	0.020				
	Zn^{2+}	1 1 0	1.18_7	0.021	6	215	2.0–6.5	0.0059
		1 1–1	-5.53_1	0.041				
	Ni^{2+}	1 1 0	1.72_4	0.015	5	174	2.6–6.2	0.0243
		1 1–1	-5.08_3	0.038				
	Co^{2+}	1 1 0	1.23_7	0.016	7	187	3.2–6.3	0.0186
		1 1–1	-5.26_3	0.026				
	Mn^{2+}	Not studied						

Literature data

Ligand	Cation	p q r	$\lg\beta_{pqr}$	Temperature/°C	I/mol dm^{-3} (medium)	Reference
1	H^+	0 1 1	6.42	25	0.1 (KNO_3)	1
		0 1 2	10.59			
		0 1 3	11.59			
	Cu^{2+}	1 1 0	5.29			
		1 1 1	8.85			
a	H^+	0 1 1	4.97	25	0.1 (KNO_3)	22
	Cu^{2+}	1 1 0	2.65			
2	H^+	0 1 1	5.85	26	0.1 (KCl)	6
2	H^+	0 1 1	5.85	25	0.1 (KCl)	23

Standard deviations used for calculating weighting factors: concentrations, 0.1%; electrode intercept, 0.1 mV; electrode slope, 0.05 mV/-lg[H] titre volume, 0.001 cm^3 emf, 0.1 mV. 2: dianion of 1-naphthyl phosphate; 3: anion of 8-quinolyl methyl phosphate; a: quinoline.

constant of the dianion of 8-quinolyl phosphate (**1**), the second protonation constant of the dianion of 1-naphthyl phosphate (**2**) or the second protonation constant of the monoanion of 8-quinolyl methyl phosphate (**3**) because the corresponding pK_a values all lie below 2, in which region the ionic strength cannot be maintained sensibly constant at 0.15 mol dm^{-3} and in which the glass electrode behaves in a non-Nernstian manner. The protonation constants found are shown in Table I, together with values reported in the literature for the same or related ligands.

The NMR spectra obtained for 8-quinolyl phosphate solutions showed a peak in the region of 3 to 7 ppm, the precise value being dependent upon pH. Figure 1 shows the chemical shift plotted against pH. It is clear that the greatest rate of change of chemical shift occurs at a pH of about 4.2, which corresponds to the less basic of the two sites for which the protonation constants have been measured by potentiometry (Table I). This implies that the potentiometrically measured pK_a value of 4.13 is to be assigned to the phosphate group. This is in direct contrast with the facile interpretation to be made by comparing the pK_a values of the three ligands, which form the subject of the present study, as given in Table I. Here the pK_a of 4.13 for 8-quinolyl phosphate is closer in value to $pK_a = 4.72$ for 8-quinolyl methyl phosphate than to $pK_a = 5.74$ for 1-naphthyl phosphate. This would imply that $pK_a = 4.13$ is assignable to the quinolinium nitrogen of 8-quinolyl phosphate. On the other hand, it is possible to rationalize the assignment of the latter pK_a to the phosphate group on the basis that the lowering of pK_a by 1.61 relative to $pK_a = 5.74$ for 1-naphthyl phosphate may be attributed to the strong electron-withdrawing character of the protonated quinolinium nitrogen atom. Perhaps the best interpretation is that the protonation constants measured for 8-quinolyl phosphate are averages of corresponding microconstants: that the first proton to be bound by ligand species **1** is effectively shared between the quinolinium nitrogen and a phosphate oxygen, possibly with the concomitant formation of hydrogen bonds.

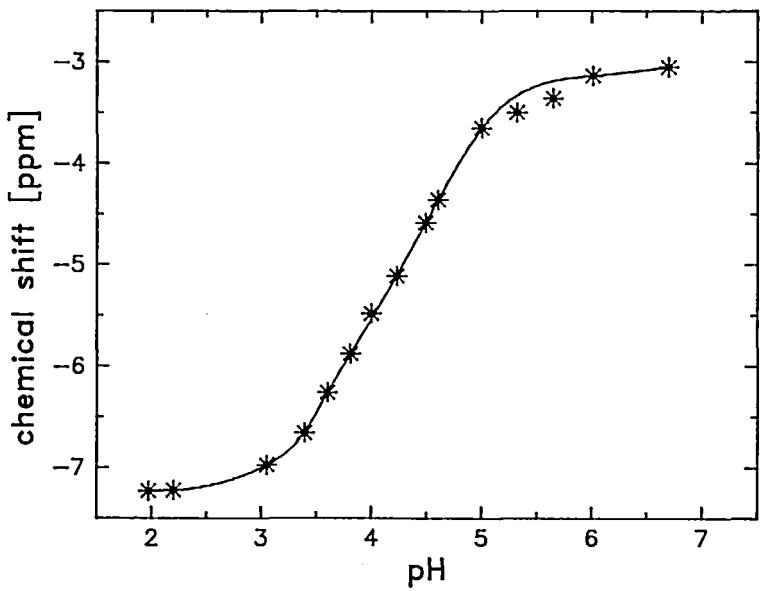

FIGURE 1 Chemical shift as a function of pH for the ^{31}P NMR titration of 8×10^{-3} mol dm^{-3} 8-quinolyl phosphate in 0.15 mol dm^{-3} NaCl.

Any interfering effects due to intermolecular stacking interactions were ruled out on the basis that the chemical shift of the phosphorus peak of 8-quinolyl phosphate was found to be independent of concentration within the range 0.002 to 0.016 mol dm^{-3}, which covers the concentration values used in the potentiometric experiments and in the NMR experiments aimed at identifying the protonation sites. The pH of the solutions in the relevant experiments was 6.2, at which level stacking interactions are likely to be strongly favoured.

Complexations

Series of titrations were carried out with total concentrations of the ligands and metals in the ranges 1 to 8 and 1 to 25 mmol dm^{-3}, respectively. Coverage of these ranges of concentrations facilitated the search for not only mononuclear binary complexes but also protonated, hydroxo- and oligonuclear species.

After subjecting the titration data obtained for each system to the computational procedures outlined above, "best" formation constants were derived. The latter are listed in Table I.

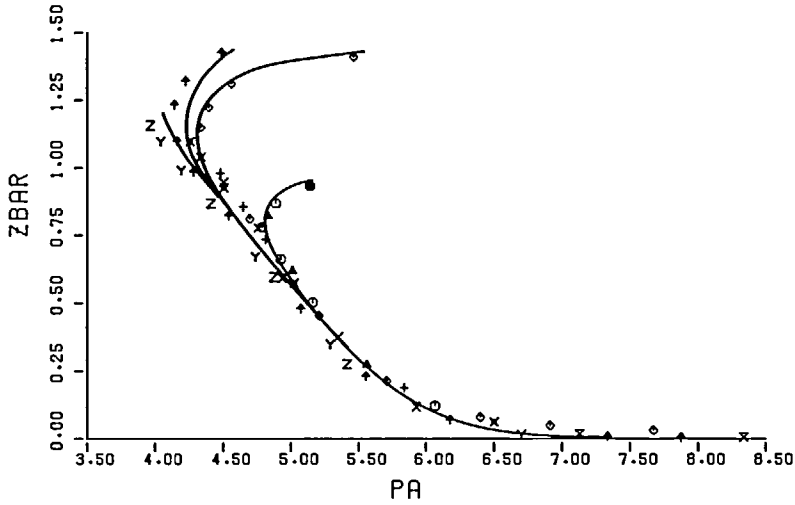

FIGURE 2 Theoretical formation curves for the 8-quinolyl phosphate–copper(II) system. Calculated from the β values of Table I and plotted with experimental ZBAR points. Concentrations /10^{-3} mol dm^{-3} of L (ligand) and M (metal) are ⊙ : 0.00331 and 0.00334, △ : 0.00331 and 0.00334, + : 0.00397 and 0.00198, X : 0.00397 and 0.00198, ◇ : 0.004098 and 0.002882, ⏃ : 0.00448 and 0.002882, $\bar{X}$: 0.002352 and 0.002672, Z : 0.004926 and 0.002968, Y : 0.004926 and 0.002968, ⊠ : 0.004926 and 0.002968.

Overlapping sets of formation curves were obtained for the systems 1-naphthyl phosphate–nickel(II), 1-naphthyl phosphate–cobalt(II), 8-quinolyl phosphate–cobalt(II) and 8-quinolyl phosphate–manganese(II) suggesting solely mononuclear binary complex formation. Indeed, the best refinements were obtained by including ML as the only metal complex in these systems. On the other hand, the formation curves obtained for all the other systems gave more complicated patterns, indicating the presence of not only mononuclear binary, but also other types of metal complex such as hydroxo species. An example is shown in Figure 2 which depicts the

formation curves obtained for the 8-quinolyl phosphate–copper(II) system. The fanning back pattern occurring towards the lower -lg[L] values is typical of systems in which hydroxo metal complexes are significant. Hydroxo metal complexation formation is also indicated by the crossing over, at pH approximately 5.4, of the deprotonation curves and the ligand protonation curve. The latter are omitted from Figure 3 for the sake of clarity. The best refinements were obtained by postulating ML and the hydroxo species, MLH_{-1}, as the only metal complexes in the systems 1-naphthyl phosphate–copper(II) and –zinc(II), 8-quinolyl phosphate–copper(II) and –nickel(II), and 8-quinolyl methyl phosphate–copper(II), –zinc(II), –nickel(II) and –cobalt(II). In the case of 8-quinolyl phosphate–zinc(II), the best-fitting chemical model was found to be ML, MLH_{-1} and MLH.

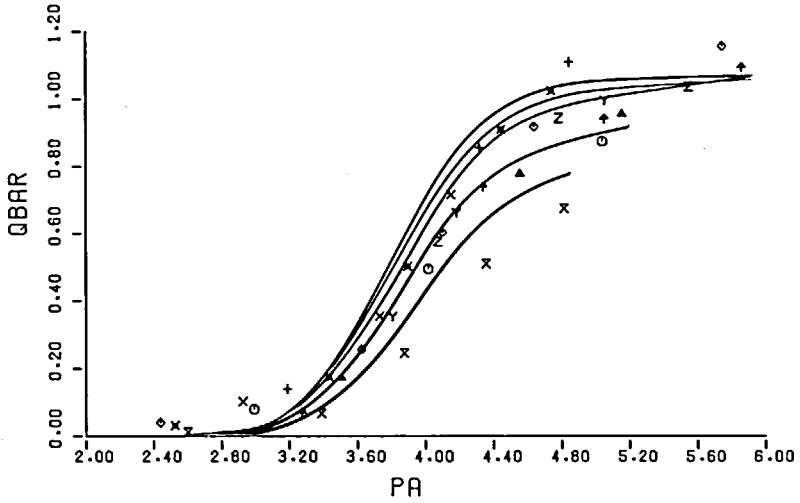

FIGURE 3 Theoretical deprotonation curves for the 8-quinolyl phosphate–copper(II) system calculated from the β values of Table I and plotted with experimental QBAR points. Concentrations /10^{-3} mol dm^{-3} of L (ligand) and M (metal) are ⊙ : 0.00331 and 0.00334, △ : 0.00331 and 0.00334, + : 0.00397 and 0.00198, X : 0.00397 and 0.00198, ◇ : 0.004098 and 0.002882, ⏃ : 0.00448 and 0.002882, $\overline{X}$: 0.002352 and 0.002672, Z : 0.004926 and 0.002968, Y : 0.004926 and 0.002968, ⊠: 0.004926 and 0.002968.

The beta values of Table I were used to generate calculated formation and deprotonation curves for each of the systems concerned. These matched the corresponding experimental and deprotonation curves well, thereby confirming the validity of the chemical model proposed in Table I for each of the systems. The respective matching is illustrated for the 8-quinolyl phosphate–copper(II) system in Figures 2 and 3. This good degree of matching is typical for the entire set of systems in Table I.

The values obtained by us for the protonation constants of 8-quinolyl phosphate and for the copper(II)–8-quinolyl phosphate, β_{110}, agree favourably with the corresponding values reported by Murakami and Sunamoto[1] (see Table I), considering the differences in supporting electrolyte and ionic strength. Although Murakami and Sunamoto propose a protonated complex, MLH, for the copper–8-quinolyl phosphate system, we could not find this species despite thorough searching and the fact that our titrations cover more extensive concentration ranges and metal:ligand

ratios. On the other hand, we found the hydroxo complex, MLH_{-1}, to occur at pH values greater than 5 in concentrations which are comparable with the ML concentrations in the pH range 3 to 7 (see Figure 5). This complex is readily rationalized through assuming proton removal to take place from one of the water molecules coordinated to the metal.

Our values for the protonation constant of 8-quinolyl methyl phosphate and β_{110} for the 8-quinolyl methyl phosphate–copper(II) complex agrees favourably with corresponding values reported by Anderegg[22] for quinoline and the quinoline–copper(II) complex, respectively. There is also favourable agreement between our value for the protonation constant of 1-naphthyl phosphate and those reported by Chanley and Feageson[6] and by Mäkitie and Mirttinen.[23]

The dianion of 1-naphthyl phosphate, the monoanion of 8-quinolyl methyl phosphate and quinoline each have only one donor atom. The first has one of the phosphate oxygens as donor, the other phosphate oxygen being a very strongly acidic centre. 8-Quinolyl methyl phosphate and quinoline each have the quinolinium nitrogen as the only donor atom. As expected, these three ligands form only weak complexes with the metals, as shown by the low values of $\lg\beta_{110}$ and by the fact that no bis or tris complexes are formed. On the other hand, the dianion of 8-quinolyl phosphate has two coordination sites and therefore has the potential of acting as a bidentate ligand. Some evidence for the realization of this potential stems from the significantly greater value obtained for $\lg\beta_{110}$ for this ligand compared with the other three ligands. Notwithstanding the latter, the complexes formed by 8-quinolyl phosphate are rather weak, as evidenced by the fairly small $\lg\beta_{110}$ values and by the fact that only mono species and no bis or tris species could be found.

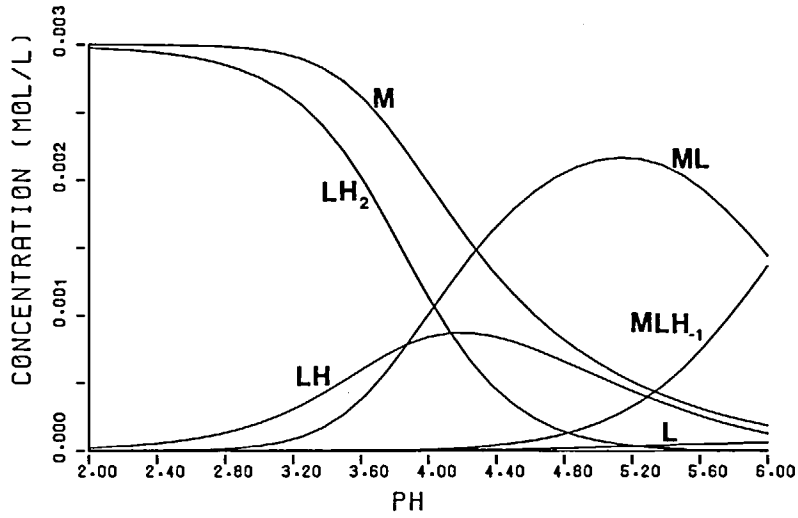

FIGURE 4 Concentration of complexes present as a function of pH for the 8-quinolyl phosphate-copper(II) system with total concentrations of L (ligand) and M (metal ion) both 3×10^{-3} mol dm^{-3}.

Murakami and Sunamoto[1] report that copper(II) ions accelerate the hydrolysis of 8-quinolyl phosphate whereas nickel(II) ions show no catalytic action. These authors postulate that a necessary condition for the catalysis is the prior formation of a

bidentate complex. Indeed, our results, in Table I, provide evidence for the formation of a chelate with coper(II) as discussed in the previous paragraph. The formation of a chelate is also indicated with nickel(II) however and, therefore, this raises the question as to what other factors may be necessary for a metal ion to catalyze the hydrolysis.

At first sight, a possible clue appears to be forthcoming by comparison with the hydrolysis of triphosphates. In this respect, Milburn *et al.*[24] have emphasized the importance of hydroxo complex formation in the dephosphorylation of adenosine-5′-triphosphate and uridine-5′-triphosphate. Further, Norman *et al.*[25] have concluded that hydrolysis of triphosphate occurs through nucleophilic attack by a coordinated hydroxide ion at one of the phosphate groups (both the triphosphate and the hydroxide are coordinated to a cobalt(III) ion). By analogy, one might reasonably anticipate that a coordinated hydroxide ion might be a necessary requirement in the metal catalyzed hydrolysis of an organic monophosphate. Indeed, as shown in figure 4, we find MLH_{-1} to be a major species in the copper(II)–8-quinolyl phosphate system. On the other hand, Figure 5 shows MLH_{-1} to occur in only small concentrations in the nickel(II)–8-quinolyl phosphate system. As it turns out, however, $CuLH_{-1}$ formation cannot be an essential requirement in the catalyzed hydrolysis of 8-quinolyl phosphate since Murakami and Sunamoto[1] report substantial catalysis by copper(II) ions in the $-\lg[H^+]$ range, 2.03 to 3.85 and, as may be seen from Figure 4, the concentration of $CuLH_{-1}$ is not significant in this range. It remains unclear, therefore, as to why copper(II) and nickel(II) ions should show such markedly different catalytic behaviour. It remains unclear, also, as to what role hydroxo complex formation has in the hydrolysis of 8-quinolyl phosphate.

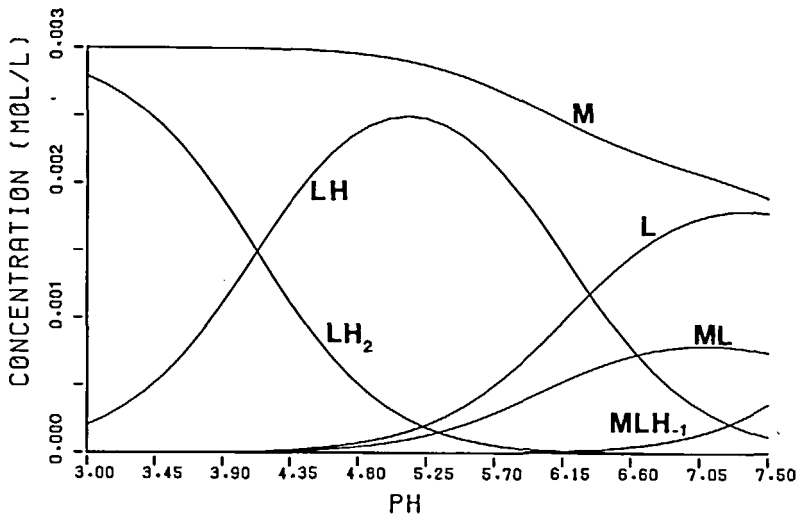

FIGURE 5 Concentration of complexes present as a function of pH for the 8-quinolyl phosphate–nickel(II) system with total concentrations of L (ligand) and M (metal ion) both 3×10^{-3} mol dm^{-3}.

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