tions. The ^1H spectra of π-$C_5H_5Mo(CO)_3SP(S)F_2$ and π-$C_5H_5Mo(CO)_2S_2PF_2$ show resonances at τ 4.29 and 4.50, respectively, which are assigned to the cyclopentadienyl groups. The ^{19}F nmr spectra may be used to assign the manner of bonding of the PS_2F_2 ligand, because phosphorus–fluorine coupling constants approximating 1200 and 1300 Hz have been assigned to unidentate and bidentate structures, respectively, in another group of transition metal complexes containing the same ligand.[1] The coupling constants and chemical shifts of π-$C_5H_5Mo(CO)_3$-$SP(S)F_2$ and $Mn(CO)_3(diphos)SP(S)F_2$, believed to possess the unidentate structure, are 1204 and 1216 Hz, respectively, and 12.4 and 13.7 ppm, respectively. The same data for $Mn(CO)_4S_2PF_2$ are 1304 Hz and -2.4 ppm consistent with the bidentate structure. It is not always safe to generalize coupling constants or even the positions of stretching frequencies in terms of unidentate of bidentate structures when comparing different sets of compounds. However, other data partially justify the structural assignments, and comparisons have been made between two series of transition metal complexes.

Acknowledgment.—The authors are grateful to Dr. William H. Graham and the Rohm & Haas Co., Redstone Research Laboratories, for the mass spectral and nmr analyses. M. L. is also grateful to Dr. Frederick A. Hartman, Proctor and Gamble Co., Miami Valley Laboratories, for helpful discussions. This work was supported, in part, by the Memphis State University Foundation.

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A Potentiometric Study of Equilibria in Aqueous Divalent Metal Orthophosphate Solutions[1]

BY C. W. CHILDS[2]

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Aqueous solutions containing potassium nitrate (0.15 mol l.$^{-1}$) and relatively small amounts of orthophosphoric acid and divalent metal nitrate have been titrated potentiometrically with potassium hydroxide at 37°. Data for each of the metal ions magnesium(II), calcium(II), zinc(II), and copper(II) have been analyzed by a least-squares method in terms of the possible formation of 1:2 and 2:2 as well as 1:1 species. To reduce the possibility of chance improvement in fit, data from three different titrations (five for magnesium(II)) have been analyzed simultaneously for each system. In each case the data are consistent with the presence in solution of the species $MH_2PO_4^+$, $MHPO_4^0$, $MH_3(PO_4)_2^-$, and $M_2H_2(PO_4)_2^0$, and, in addition, MPO_4^- in the case of magnesium(II). Approximate values for the equilibrium constants expressed as concentration quotients for 0.15 mol l.$^{-1}$ of potassium nitrate of these species are presented. Possible structures for $MH_3(PO_4)_2^-$ and $M_2H_2(PO_4)_2^0$ in solution are similar to arrangements in solid divalent metal orthophosphates.

Introduction

Knowledge of the interactions between divalent metal ions and orthophosphate anions in aqueous solutions is pertinent to the study of many natural systems. Of the previous equilibrium studies[3,4] of these interactions, most have been concerned with the determination of the equilibrium constant of the species $MHPO_4^0$ (where M is a divalent metal ion—usually calcium(II) or magnesium(II)) and sometimes $MH_2PO_4^+$. In one study[4] of calcium orthophosphate solutions an equilibrium constant for $CaPO_4^-$ was obtained.

In all such studies the assumption has been made that only 1:1 metal ion–orthophosphate species are formed. However the evidence for the dimeric species $H_5(PO_4)_2^-$,[5–7] $H_4(PO_4)_2^{2-}$, and $H_3(PO_4)_2^{3-}$ [7] in orthophosphate solutions suggested the possibility of the existence of 1:2 and 2:2 species in divalent metal orthophosphate solutions. Gardner and Glueckauf have recently shown[8] that the formation of 1:2 or 2:1 (or both) and 2:2 species is consistent with osmotic coefficient data for the sulfates of magnesium(II), calcium(II), zinc(II), nickel(II), and copper (II) in aqueous solution.

The present paper reports pH measurements at 37° with the cell

$$\text{glass electrode}|H_3PO_4\ (c_1),\ M(NO_3)_2\ (c_2),\ KOH\ (c_3),\ KNO_3\ (0.15\ \text{mol l.}^{-1})|KCl(\text{satd})|\text{calomel electrode}$$

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[2] Correspondence should be addressed to the author at the Canada Centre for Inland Waters, Box 5050, Burlington, Ontario, Canada.

[3] "Stability Constants," Special Publication No. 7, The Chemical Society, London, 1958.

[4] A. Chughtai, R. Marshall, and G. H. Nancollas, *J. Phys. Chem.*, **72**, 208 (1968).

[5] M. Selvaratnam and M. Spiro, *Trans. Faraday Soc.*, **61**, 360 (1965).

[6] K. L. Elmore, J. D. Hatfield, R. L. Dunn, and A. D. Jones, *J. Phys. Chem.*, **69**, 3520 (1965).

[7] C. W. Childs, *ibid.*, **73**, 2956 (1969).

[8] A. W. Gardner and E. Glueckauf, *Proc. Roy. Soc., Ser. A*, **313**, 131 (1969).

where c_1, c_2, and c_3 are small compared with 0.15 mol l.$^{-1}$, and M represents each of the metal ions magnesium(II), calcium(II), zinc(II), and copper(II). The pH ranges extend from 3.0 in each case to 8.5 for magnesium(II), to 6.6 for calcium(II), to 5.0 for zinc(II), and to 4.4 for copper(II), the upper limits being determined by the onset of precipitation.

Experimental Section

Materials and Solutions.—Stock orthophosphoric acid,[7] potassium nitrate,[9] potassium hydroxide,[9] and copper(II) nitrate solutions were prepared as previously described. The stock zinc(II) nitrate (Baker Analyzed reagent), magnesium(II) nitrate (Ajax Univar), and calcium(II) nitrate (Ajax Univar) solutions were standardized by EDTA titrations. Erio T indicator[10] was used for the zinc(II) and magnesium(II) determinations and thymolphthalein complexone[11] for calcium(II). The zinc(II) and copper(II) nitrate solutions were made slightly acid with nitric acid to repress hydrolysis.

Analar potassium hydrogen phthalate and sodium tetraborate were used without further purification for the preparation of 0.05 mol l.$^{-1}$ standard buffer solutions (pH values 4.029 and 9.082, respectively,[12] at 37°).

All critical concentrations are expressed in moles per liter at 37.°

Potentiometric Measurements.—All measurements were made at 37° with the apparatus and procedure previously described.[7,9] The precision of all pH measurements was estimated from duplicate titrations to be about ±0.005 pH unit. In all cases the standard buffer readings after a titration agreed within 0.005 pH unit with the initial settings.

Data.—The pH titrations are summarized in Table I.[13] The upper limits of each titration were determined by precipitation from solution as indicated by a downward drift of the pH reading and the subsequent appearance of a fine suspension in the solution.

In addition, two titrations, similar to those described above but in the absence of orthophosphoric acid, were performed for both zinc(II) nitrate and copper(II) nitrate in order to determine the metal ion hydrolysis constants. In these titrations the metal ion concentrations were close to 5×10^{-3} and 1×10^{-2} mol l.$^{-1}$ and the overall pH ranges were 3.2–5.6 for copper(II) and 6.0–7.1 for zinc(II).

Interpretation of Data

The data were interpreted with the aid of the computer program SCOGS[14] as previously described.[7,9] This program uses an iterative least-squares method to find the best match between the observed and calculated titers by refining the estimated values of the equilibrium constants for a postulated set of equilibria.

For the solution of mass balance equations, $[H^+]$ was estimated from the pH values by[15] $p[H] = pH + \log F$. The factor, F, may be considered to allow for the activity coefficient of hydrogen ions, the residual liquid junction potential, and any other systematic errors in the pH measurements.[9] Previously, in analyzing data obtained from identical measurements on other systems, ranges of F values were used, consistent with the minima in a residual least-squares parameter as F was varied. These ranges were 0.72–0.82 for some amino acid and metal ion–amino acid systems[9] and, subsequently, 0.75–0.90 for the orthophosphate system.[7]

Table I

Summary of pH Titration Data[a]

10^3M, mol l.$^{-1}$	10^3L, mol l.$^{-1}$	pH range	N
	(1) Calcium(II)		
5.2	6.0	3.1–6.6	12
4.6	9.6	3.1–6.6	18
8.1	8.4	3.0–6.2	12
	(2) Magnesium(II)		
0.92	0.96	3.1–8.0	22
3.4	6.0	3.0–8.0	32
5.7	6.0	3.0–7.4	29
4.6	9.6	3.0–8.5	32
8.0	8.4	3.1–7.0	22
	(3) Zinc(II)		
2.8	6.0	3.0–5.0	17
4.1	3.0	3.0–4.9	20
6.9	9.0	3.0–4.6	16
	(4) Copper(II)		
3.2	6.0	3.0–4.4	13
4.7	3.0	3.1–4.3	17
7.9	9.0	3.1–4.0	14

[a] Rounded initial concentrations of total metal ion (M) and orthophosphate (L), pH range, and number of readings (N) for each titration.

Recently, McBryde has described[16] a simple direct determination of a factor Γ $(=H/[H])$, which is formally identical with F. His method is to determine the pH of a solution containing a known small concentration of strong acid under the same conditions of background electrolyte and temperature as those for the test solutions. Then, assuming that the strong acid is completely dissociated, F (or Γ) may be determined from the known [H] and the observed H. This factor can then be applied to calculate values of [H] for the test solutions. In the present work the pH values of solutions containing small known quantities of nitric acid and 0.15 mol l.$^{-1}$ of potassium nitrate were measured at 37°. Two series of measurements were made—one involved single pH measurements on separate solutions; the other, the titration of a 0.15 mol l.$^{-1}$ potassium nitrate solution (after flushing with nitrogen for 2 hr) with 0.5 mol l.$^{-1}$ of nitric acid. Results from both series were in close agreement. Those from the titration are shown in Table II.

The small drift in the value of F with pH is probably not significant as there is difficulty in defining [H], and hence F, above pH 4.[16] In the present work it has been assumed that F lies in the range 0.80–0.85 and calculations have been carried out for both $F = 0.80$ and $F = 0.85$.

The equilibrium constants are defined below in forms

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(9) C. W. Childs and D. D. Perrin, *J. Chem. Soc. A*, 1039 (1969).

(10) A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, Longmans, Green and Co., London, 1961.

(11) J. Körbl and R. Přibil, *Collect. Czech. Chem. Commun.*, **23**, 1213 (1958).

(12) D. J. Alner, J. J. Greczek, and A. G. Smeeth, *J. Chem. Soc. A*, 1205 (1967).

(13) For complete titration data order Document No. NAPS-01077 from ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022, remitting $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

(14) I. G. Sayce, *Talanta*, **15**, 1397 (1968).

(15) Note that in previous papers[7,9] this equation was inadvertently written $p[H] = pH - \log F$.

(16) W. A. E. McBryde, *Analyst (London)*, **94**, 337 (1969).

TABLE II

DETERMINATION OF F ($=H/[\mathrm{H}]$)[a]

Titer	pH	F	Titer	pH	F
0.004	4.489	0.81	0.06	3.302	0.83
0.006	4.312	0.81	0.09	3.126	0.83
0.008	4.186	0.81	0.13	2.967	0.83
0.010	4.090	0.81	0.17	2.850	0.83
0.013	3.972	0.82	0.22	2.739	0.83
0.017	3.854	0.82	0.30	2.605	0.83
0.022	3.740	0.82	0.38	2.504	0.83
0.03	3.605	0.82	0.45	2.430	0.83
0.04	3.480	0.82	0.50	2.385	0.83

[a] Initial conditions: potassium nitrate, 0.15 mol l.$^{-1}$; volume, 50.21 ml; 37°; titrant, nitric acid, 0.5054 mol l.$^{-1}$.

which involve (H^+) = $10^{-\mathrm{pH}}$ and the concentrations (denoted by brackets) of all other species. Although "cumulative" constants are determined with the program, they are given here, for convenience, as "single-step" constants with the exception of (8).

$$K_{a1} = [H_2PO_4^-](H^+)/[H_3PO_4^0] \quad (1)$$

$$K_{a2} = [HPO_4^{2-}](H^+)/[H_2PO_4^-] \quad (2)$$

$$K_{a3} = [PO_4^{3-}](H^+)/[HPO_4^{2-}] \quad (3)$$

$$K(H_5(PO_4)_2^-) = [H_5(PO_4)_2^-]/[H_3PO_4^0][H_2PO_4^-] \quad (4)$$

$$K(H_4(PO_4)_2^{2-}) = [H_4(PO_4)_2^{2-}]/[H_2PO_4^-]^2 \quad (5)$$

$$K(H_3(PO_4)_2^{3-}) = [H_3(PO_4)_2^{3-}]/[H_2PO_4^-][HPO_4^{2-}] \quad (6)$$

$$^*K_1 = [MOH^+](H^+)/[M^{2+}] \quad (7)$$

$$^*\beta_{2,2} = [M_2(OH)_2^{2+}](H^+)^2/[M^{2+}]^2 \quad (8)$$

$$K_{m,1} = [MH_2PO_4^+]/[M^{2+}][H_2PO_4^-] \quad (9)$$

$$K_{m,2} = [MHPO_4^0]/[M^{2+}][HPO_4^{2-}] \quad (10)$$

$$K_{m,3} = [MPO_4^-]/[M^{2+}][PO_4^{3-}] \quad (11)$$

$$K_{m1,2} = [MH_3(PO_4)_2^-]/[MH_2PO_4^+][HPO_4^{2-}] \quad (12)$$

$$K_{m2,m2} = [M_2H_2(PO_4)_2^0]/[MHPO_4^0]^2 \quad (13)$$

Previously determined values[7] for the equilibrium constants of eq 1–6 were used here and they are given in Table III for convenience.

TABLE III

EQUILIBRIUM CONSTANTS FOR REACTIONS BETWEEN HYDROGEN IONS AND ORTHOPHOSPHATE ANIONS (0.15 MOL L.$^{-1}$ OF POTASSIUM NITRATE, 37°)

	$F = 0.80$	$F = 0.85$
pK_{a1}	1.92	2.02
pK_{a2}	6.70	6.70
pK_{a3}	11.30	11.27
Log $K(H_5(PO_4)_2^-)$	1.58	1.15
Log $K(H_4(PO_4)_2^{2-})$	0.72	0.76
Log $K(H_3(PO_4)_2^{3-})$	0.38	0.45

Although metal ion hydrolysis might be expected to be small in the solutions studied here, it has been included for the sake of completeness using the values shown in Table IV. For zinc(II) and copper(II) the values derived from the titrations in the absence of orthophosphate are shown, while for magnesium(II) and calcium(II) the values were taken from the results of a previous study[17] of amino acid complex formation by these metal ions. The standard deviations derived from the least-squares method used in the computer program are given in parentheses. The values in Table IV appear reasonable in comparison with literature values[3] determined under different conditions of temperature and background electrolyte. The species $Cu_3(OH)_4^{2+}$, for copper(II), and the species $Zn_2(OH)_2^{2+}$, for zinc(II), were also tried in the interpretations, but they proved inconsistent with the data. As before,[7,9] inconsistency was taken to be demonstrated when the value of the constant estimated for a postulated equilibrium was progressively decreased without convergence in the iteration process and the calculated concentration of the species became negligible.

TABLE IV

HYDROLYSIS CONSTANTS OF THE METAL IONS (0.15 MOL L.$^{-1}$ OF POTASSIUM NITRATE, 37°)

	Log $^*K_1$		Log $^*\beta_{2,2}$	
	$F = 0.80$	$F = 0.85$	$F = 0.80$	$F = 0.85$
Mg(II)	11.5 (0.3)	11.4 (0.3)	...	...
Ca(II)	11.7 (0.3)	11.6 (0.3)	...	...
Zn(II)	9.03 (0.02)	9.03 (0.02)	...	...
Cu(II)	7.6 (0.3)	7.7 (0.2)	10.49 (0.08)	10.45 (0.04)

Values from Tables III and IV *for the appropriate assumed value of F* were used to account for equilibria 1–8. Hence the data in Table I were used to determine only the values of the constants in eq 9–13.

The ionic activity product of water was taken to be $10^{-13.62}$ at 37°.[18] It should be noted that since, in SCOGS, $[H^+][OH^-]F^2$ is equated with $[H^+][OH^-]\cdot f_Hf_{OH}$, where f_H and f_{OH} are the true thermodynamic activity coefficients, an error is introduced when $F^2 \neq f_Hf_{OH}$. However, calculations showed that this inequality would not be significant in analyzing data for the pH ranges studied here.

Initially, the only metal ion orthophosphate species postulated was $MHPO_4^0$. The equilibrium constants obtained with this assumption and with F set equal to 0.80 are shown in parentheses in Table V. Subsequently, the species $MH_2PO_4^+$, MPO_4^-, $MH_4(PO_4)_2^0$, $MH_3(PO_4)_2^-$, ..., $M_2H_4(PO_4)_2^{2+}$, ... were added successively to the interpretation until all of the possible 1:1, 1:2, and 2:2 species (13 in all) had been tried. For all four metal ions the species $MH_2PO_4^+$, $MHPO_4^0$, $MH_3(PO_4)_2^-$, and $M_2H_2(PO_4)_2^0$ were consistent with the data. The addition of each of these species produced an improvement in the least-squares fit to the data and the estimates of the corresponding equilibrium constants converged to apparently reasonable values. In addition, for magnesium(II), the species MPO_4^- fell into this category but presumably because of the onset of precipitation at lower pH values (see Table I) MPO_4^- was not consistent with the data for the other three metal ions.

Table V lists the refined values of the equilibrium constants for $F = 0.80$ and $F = 0.85$. Limits shown are the sums of the standard deviations of the cumulative equilibrium constants (as refined by the computer program) used in obtaining the values. These are probably satisfactory for comparative purposes within the table. The standard deviation in titer[14] (sdt) is a

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(17) C. W. Childs, unpublished results.

(18) H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

TABLE V

EQUILIBRIUM CONSTANTS FOR METAL ION–ORTHOPHOSPHATE COMPLEXES (0.15 MOL L.$^{-1}$ OF POTASSIUM NITRATE, 37°)

	Magnesium(II)		Calcium(II)	
	$F = 0.80$	$F = 0.85$	$F = 0.80$	$F = 0.85$
Log $K_{m,1}$	0.7 ± 0.3	0.4 ± 0.2	0.6 ± 0.3	0.5 ± 0.4
Log $K_{m,2}$	1.8 ± 0.1 (1.8 ± 0.1)	1.8 ± 0.1	1.3 ± 0.2 (1.7 ± 0.1)	1.3 ± 0.2
Log $K_{m,3}$	3.4 ± 0.1	3.3 ± 0.1	. . .	. . .
Log $K_{m1,2}$	2.3 ± 0.5	2.6 ± 0.4	2.4 ± 0.8	2.5 ± 0.9
Log $K_{m2,m2}$	1.4 ± 0.4	1.4 ± 0.2	3.7 ± 0.6	3.7 ± 0.9
10^4(sdt), ml	15.6 (16.4)	6.6	14.4 (20.5)	14.6

	Zinc(II)		Copper(II)	
	$F = 0.80$	$F = 0.85$	$F = 0.80$	$F = 0.85$
Log $K_{m,1}$	1.2 ± 0.1	1.1 ± 0.1	1.3 ± 0.1	1.1 ± 0.1
Log $K_{m,2}$	2.4 ± 0.1 (2.6 ± 0.1)	2.3 ± 0.1	3.3 ± 0.1 (3.4 ± 0.1)	3.2 ± 0.1
Log $K_{m1,2}$	2.8 ± 0.5	3.1 ± 0.4	3.4 ± 0.4	3.9 ± 0.2
Log $K_{m2,m2}$	3.6 ± 0.3	3.7 ± 0.3	2.6 ± 0.3	2.3 ± 0.6
10^4(sdt), ml	3.9 (9.9)	4.1	3.9 (11.7)	3.7

measure of the ability of the refined values to reproduce the experimental data.

The values obtained for $F = 0.80$ are not significantly different from those for $F = 0.85$. Calculations were carried out for $F = 0.75$ and $F = 0.90$, and for each of the four systems the minimum in the sdt *vs.* F plot occurred between $F = 0.80$ and $F = 0.85$, consistent with the estimate obtained from the use of McBryde's method (see Table II).

Discussion

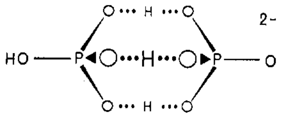
Gardner and Glueckauf[8] have recently interpreted osmotic coefficient data for several divalent metal sulfates in terms of the formation of "ion pairs, triplets, and quadruplets." Their triplet, $M(SO_4)_2^{2-}$, and quadruplet, $M_2(SO_4)_2^0$, which appear to be significant at salt concentrations as low as 5×10^{-3} mol l.$^{-1}$, are analogous to the species $MH_3(PO_4)_2^-$ and $M_2H_2(PO_4)_2^0$ postulated in the present work. They found a parallelism between the "infinite dilution" 1:1 equilibrium constants of metal ion sulfates and nitrates (Ca(II) > Cu(II) > Mg(II) > Co(II) > Zn(II)), and this was interpreted in terms of a specific, but similar, interaction, independent of the anionic charge, between oxyanions and divalent cations. However, the "0.15 mol l.$^{-1}$ potassium nitrate" equilibrium constants for $MHPO_4^0$ (and for $MH_2PO_4^+$ although the limits overlap) lie in the order Cu(II) > Zn(II) > Mg(II) > Ca(II), which is that usually observed[3] in the formation of complexes of relatively high stability. Since the "infinite dilution" equilibrium constants would probably lie in the same order, it seems that HPO_4^{2-} (and probably $H_2PO_4^-$) behave differently from SO_4^{2-} and NO_3^- with respect to interaction with metal ions. An explanation is that the primary hydration sphere of the cation, which is apparently so important for SO_4^{2-} and NO_3^-, has less influence on the interaction of HPO_4^{2-} and $H_2PO_4^-$ with metal ions.

This difference in behavior is also indicated by Raman spectral measurements which suggest that while calcium(II)[19] and copper(II)[20] form contact, probably unidentate, complexes with nitrate in aqueous solutions, magnesium(II)[21] and zinc[19] do not (except in solutions of very low water content). In contrast zinc(II) is considered to be able to form bidentate contact complexes through two of the oxygen atoms bound to one of the phosphorus atoms of diphosphate.[22] Similar information on the nature of metal ion orthophosphate interactions would be of interest.

The possibility of fortuitous improvements in fit to the data as the number of postulated equilibria is increased cannot be completely discounted and it is possible that use of a different criterion of best match would lead to different results. However, in this and similar[7,9] work, an apparently high degree of discrimination in the selection of equilibria has been obtained. In the present work, although 13 metal ion–orthophosphate species were tested, only the same four proved consistent with the data for calcium(II), zinc(II), and copper(II). For magnesium(II) the presence of the further species, MPO_4^-, is readily explained by the acquisition of data at higher pH values. Moreover the values obtained for the formation quotients appear reasonable when literature values[3,4] are available for comparison.

The structure of the 1:2 and 2:2 species is of interest. The ability of an oxygen atom to form a strong hydrogen bond in a –P–O situation is known.[23] The species $H_5(PO_4)_2^-$, $H_4(PO_4)_2^{2-}$, and $H_3(PO_4)_2^{3-}$ probably each involve three hydrogen bonds[7] (see I). $MH_3(PO_4)_2^-$ and $M_2H_2(PO_4)_2^0$ each contain the same number of cations as $H_4(PO_4)_2^{2-}$ and similar structures can be drawn for species I–III. Hydrogen bonds are represented by ···H···, while M--O represents a metal ion adjacent to an oxygen of a tetrahedral orthophosphate group. The possibility that the metal ions were adjacent to the extreme oxygens was excluded on the basis of measurements[17] similar to those described here on solutions of L-serine orthophosphate in the presence of each of the metal ions calcium(II) and magnesium(II). The data for both of these systems were consistent with the presence of 1:2 and 2:2 species analogous to those discussed here. Since in L-serine orthophosphate both extreme oxygens are involved in the serine linkage, it is likely that the metal ions are associated with the central

I



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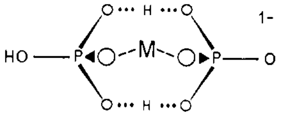

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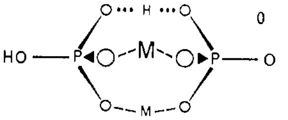

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(19) D. E. Irish, A. R. Davis, and R. A. Plane, *J. Chem. Phys.*, **50**, 2262 (1969).

(20) A. R. Davis, Ph.D. Thesis, University of Waterloo, Waterloo, Canada, 1967.

(21) D. E. Irish, G. Chang, and D. L. Nelson, *Inorg. Chem.*, **9**, 425 (1970).

(22) H. Brintzinger and R. A. Plane, *ibid.*, **6**, 623 (1967).

(23) See, for example, D. E. C. Corbridge in "Topics in Phosphorus Chemistry," Vol. 3, Interscience, New York, N. Y., 1966, p 220.

TABLE VI

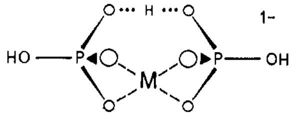
CALCULATED COMPOSITIONS OF A SOLUTION CONTAINING 0.008 MOL L.$^{-1}$ OF ORTHOPHOSPHATE, 0.008 MOL L.$^{-1}$ OF CALCIUM(II), AND 0.15 MOL L.$^{-1}$ OF POTASSIUM NITRATE AT 37°[a]

					[Orthophosphate] as					[Orthophosphate] as	
pH	$[Ca^{2+}]$	$[H_3PO_4]$	$[H_2PO_4^-]$	$[HPO_4^{2-}]$	$H_5(PO_4)_2^-$	$H_4(PO_4)_2^{2-}$	$H_3(PO_4)_2^{3-}$	$[CaH_2PO_4^+]$	$[CaHPO_4^0]$	$CaH_3(PO_4)_2^-$	$Ca_2H_2(PO_4)_2^0$
3.0	779	54	652	*	27	46	*	21	*	*	*
3.5	778	18	697	*	10	52	*	22	*	*	*
4.0	777	6	712	1	3	54	*	23	*	*	*
4.5	776	2	714	4	1	54	*	23	1	1	*
5.0	774	1	705	14	*	53	*	22	2	2	*
5.5	767	*	672	42	*	48	1	21	6	5	3
6.0	737	*	578	115	*	36	3	18	16	11	24
6.5	664	*	390	246	*	16	5	11	31	15	87
7.0	585	*	192	381	*	4	3	5	42	10	163

[a] $10^5 \times$ concentrations in mol l.$^{-1}$; concentrations less than 5×10^{-6} mol l.$^{-1}$ are shown by an asterisk.

oxygens. Alternative forms for II and III are IIa and IIIa. Such structures are idealistic since consideration of the solvent molecules is omitted and they probably represent only the most stable of a number of configurations contributing to the properties of the solution. However the linkage shown in III, involving two metal ions and one hydrogen bond, is similar to that between adjacent tetrahedra in solid calcium monohydrogen orthophosphate;[24] the linkage in IIa binds adjacent tetrahedra in barium monohydrogen orthophosphate,[25] and the linkage shown in IIIa is present in calcium dihydrogen orthophosphate monohydrate.[26]

IIa



IIIa

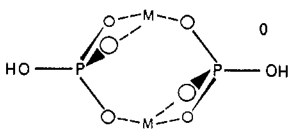


Table VI lists the calculated composition of a solution containing 0.008 mol l.$^{-1}$ of calcium(II), 0.008 mol l.$^{-1}$ of orthophosphate, and 0.15 mol l.$^{-1}$ of potassium nitrate as the pH varies from 3.0 to 7.0. The values in Tables III–V for $F = 0.80$ have been used in the calculations. For none of the pH values shown were $[PO_4^{3-}]$ or $[CaOH^+]$ greater than 5×10^{-6} mol l.$^{-1}$.

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[24] G. MacLennan and C. A. Beevers, *Acta Crystallogr.*, **8**, 579 (1955).

[25] R. C. L. Mooney, Report TID-5212, U. S. Atomic Energy Commission, Washington, D. C., Sept 1955, p 165.

[26] G. MacLennan and C. A. Beevers, *Acta Crystallogr.*, **9**, 187 (1956).

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Binding Energy of the "2p" Electrons[1] of Silicon in Various Compounds

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The binding energy of the "2p" electrons[1] of silicon in 16 compounds was measured by means of photoelectron spectroscopy. It was found that the binding energy for this orbital ranged from *ca.* 107 eV for Na_2SiF_6, in which the silicon atom is surrounded by strongly electron-withdrawing atoms, to *ca.* 99 eV for the element. These values are discussed from the viewpoint of the influence of the atoms directly bonded to the silicon. In addition, the binding energies for the "2p" orbitals of silicon, phosphorus, and sulfur have been correlated through structures having identical surrounding atoms. Interpretation of these experimental results has been aided by atomic SCF calculations on several configurations of silicon, phosphorus, and sulfur.

Photoelectron spectroscopy of electrons in inner-shell orbitals offers considerable promise as a physical tool for chemical investigations. Indeed, the forerunners[3] in this field have seen fit to apply the acronym ESCA to it, where ESCA stands for electron spectroscopy for chemical analysis.

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[1] The designation of the atomic orbital for which a binding energy is measured is put in quotation marks, *e.g.*, "2p," since the inner orbitals of molecules are somewhat delocalized and hence are not identical with the corresponding atomic inner orbitals.

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[3] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, *Nova Acta Regiae Soc. Sci. Upsal.*, [4] **20** (1967).