Table III

Stability Constants of the Monoglycinate Complexes

Ion	Temp, °C 0	11	25	40	55
Ce	2.2 ± 0.5[a]	...	3.4 ± 0.4	5.0 ± 0.6	5.7 ± 0.6
Pm	2.8 ± 0.3	3.3 ± 0.7	4.7 ± 0.3	6.2 ± 0.5	...
Eu	4.1 ± 0.3		5.0 ± 0.3	6.0 ± 0.4	8.0 ± 0.3
Am	3.0 ± 0.4	3.7 ± 0.1	4.9 ± 0.2	6.0 ± 0.3	...
Cm	4.2 ± 0.2	4.6 ± 0.6	6.4 ± 0.2	8.9 ± 0.3	...

[a] The error assigned is twice the standard deviation (2σ).

The results of the calculation of enthalpy values from the temperature differential method are given in Table IV with values of ΔG and ΔS. In all cases the enthalpy is positive and, hence, opposed to complexation. These endothermic values are larger than for the monoacetate complexing[7] and comparable to the monoisobutyrate data.[8] The driving force for the complex formation is the positive entropy which is comparable to that of the monocarboxylate complexes. The similarity of the ΔH and ΔS values to those for the simple carboxylate anions, in contrast to the disagreement with the values for the α-hydroxycarboxylate complexes,[7,9] leads to the conclusion that the glycinate zwitterion forms inner-sphere, monodentate complexes with the trivalent lanthanide and actinide ions. The agreement between the entropy values of the acetate and glycinate complexing indicates that the effect on the hydration of the cation is comparable. Consequently, the lower stability of the glycinate complexes as determined by the more endothermic enthalpy is probably due to decreased ionic attraction in the zwitterion complex $M^{3+}\cdots{}^{-}O_2CCH_2NH_3^+$ than in the acetate where the ligand positive charge is absent, $M^{3+}\cdots{}^{-}O_2CCH_3$.

Table IV

Thermodynamic Parameters for the Monoglycinate Complexes at 25.0° and $\mu = 2.0\ M$ ($NaClO_4$)

Ion	ΔG, kcal mol^{-1}	ΔH, kcal mol^{-1}	ΔS, cal deg^{-1} mol^{-1}
Ce	0.75 ± 0.03	3.3 ± 0.4	14 ± 2
Pm	0.91 ± 0.03	3.5 ± 0.4	15 ± 2
Eu	0.99 ± 0.02	2.3 ± 0.4	11 ± 2
Am	0.93 ± 0.02	2.9 ± 0.4	13 ± 2
Cm	1.12 ± 0.02	3.3 ± 0.4	15 ± 2

Acknowledgment.—This research was supported by the U. S. Atomic Energy Commission under Contract AT-(40-1)-1797. We wish to thank Mr. Jose L. Vinelli for valuable assistance with the experimental work.

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Metal Complexes of Nonamethylimidodiphosphoramide

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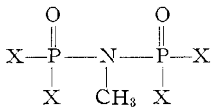
Complexes of nonamethylimidodiphosphoramide, $[(CH_3)_2N]_2P(O)N(CH_3)P(O)[N(CH_3)_2]_2$, with both transition and nontransition metal perchlorates have been prepared. The coordinating ability of nonamethylimidodiphosphoramide (NIPA) is quite similar to that of octamethylpyrophosphoramide (OMPA). Infrared evidence is in agreement with the formation of a six-membered chelate ring between the phosphoryl oxygens of NIPA and the metal ions. The Dq value of NIPA toward Ni(II) is the same as that for OMPA (726 *vs.* 727 cm^{-1}) while the β° value for NIPA with Ni(II) is lower (9.7 *vs.* 11.1%). The substitution of the N-methyl group for the bridge oxygen of OMPA appears to have little effect on the stability of the complexes.

Introduction

Donoghue and Drago[2] prepared a series of metal complexes of hexamethylphosphoramide (HMPA). The infrared data for these complexes are in support of coordination of the metal ions to the phosphoryl oxygen atom of the ligand. The transition metal perchlorate complexes isolated by them were generally four-coordinate and spectral data were indicative of tetrahedral geometry.

We have found that octamethylpyrophosphoramide (OMPA) is a very versatile bidentate ligand.[3] This ligand can be pictured as two HMPA molecules combined through a P–O–P linkage which has replaced one dimethylamino group on each HMPA molecule. OMPA acts as a bidentate ligand utilizing both phosphoryl oxygen atoms. Recent X-ray studies[4] have confirmed the previously proposed[3] six-membered chelate ring which is formed between the metal ions and the pyrophosphate linkage of OMPA. The high stability of these complexes was attributed to the chelate effect.

The purpose of the present study was to examine the coordinating ability of the ligand obtained by replacing the P–O–P oxygen atom with an N-methyl group. The resulting ligand, nonamethylimidodiphosphoramide (NIPA)



$$\mathrm{X{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle X}{|}}{P}}{-}\underset{\underset{\displaystyle CH_3}{|}}{N}{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle X}{|}}{P}}{-}X}$$

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[1] NASA Predoctoral Fellow.
[2] J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2**, 1158 (1963).
[3] M. D. Joesten, *ibid.*, **6**, 1598 (1967).
[4] M. D. Joesten and P. G. Lenhert, to be submitted for publication.

where $X = N(CH_3)_2$, forms complexes with both transition and nontransition metals which show no signs of decomposition after standing in a desiccator for several months. The preparation and characterization of these complexes will be reported in this paper.

Experimental Section

Reagents.—Nonamethylimidodiphosphoramide was prepared by a reported method.[5] The preparation involved the sequence of reactions

$$[(CH_3)_2N]_2P(O)Cl + 2CH_3NH_2 \longrightarrow [(CH_3)_2N]_2P(O)N(CH_3)H + CH_3NH_3Cl \quad (1)$$

$$[(CH_3)_2N]_2P(O)N(CH_3)H + Na \longrightarrow [(CH_3)_2N]_2P(O)N(CH_3)Na + {}^1/_2H_2 \quad (2)$$

$$[(CH_3)_2N]_2P(O)N(CH_3)Na + [(CH_3)_2N]_2P(O)Cl \longrightarrow \text{NIPA} + NaCl \quad (3)$$

Pentamethylphosphoramide in reaction 1 was prepared by a reported procedure.[6] N,N′,N″,N‴-Tetramethylphosphordiamidic chloride, $[(CH_3)_2N]_2P(O)Cl$, was obtained from K & K Laboratories, Inc. Nonamethylimidodiphosphoramide was purified by fractional distillation and the fraction which boiled in the range 135–137° at 0.15 mm was collected. The ligand is very hygroscopic and a good melting point was difficult to obtain. The melting point range was 50–58° compared to a reported value of 58°.

Preparation of Complexes.—All of the complexes except those of $Hg(ClO_4)_2$, $Th(ClO_4)_4$, $UO_2(ClO_4)_2$, and the tris complex of $Cu(ClO_4)_2$ were prepared by the following method. The hydrated metal perchlorates were dehydrated by stirring with excess 2,2′-dimethoxypropane. Enough ligand was added in an acetone solution to give slightly more than a 3:1 ratio of ligand to dehydrated metal salt. Precipitation of the complex began as soon as the solutions were well mixed. Precipitation was completed by addition of excess anhydrous ether. The solution was decanted from the complex and a few milliliters of acetone was added. The mixture was shaken and anhydrous ether was again added to reprecipitate any complex which dissolved. This acetone–ether wash was repeated about four or five times. The complex was then collected on a filter and washed with anhydrous ether under a nitrogen blanket. The filtered product was then dried *in vacuo* for about 12 hr.

The tris complex of $Cu(ClO_4)_2$ was prepared by adding ligand (0.005 mol) to a solution of the hydrated salt (0.001 mol) in 15 ml of acetone. The volume of the solution was then reduced almost to dryness either with a water aspirator or by blowing nitrogen over the solution. The complex formed as colorless crystals. The complex was washed thoroughly with ether and then dried *in vacuo*.

The complexes of $Hg(ClO_4)_2$ and $UO_2(ClO_4)_2$ were prepared in the same manner as above except that 2,2′-dimethoxypropane was not used. The hydrated salts were dissolved in acetone or methanol and the rest of the previous procedure was followed.

The $Th(ClO_4)_4$ complex was prepared by dissolving the hydrated salt in acetone and then enough ligand in acetone solution was added to give slightly more than 4:1 ratio of ligand to salt. A white gummy solid remained after stirring. This solid was kneaded with a stirring rod in an excess of anhydrous ether. Several portions of ether were used, and the kneading was continued until a white powder remained. The white powder was collected on a filter and washed with ether under a nitrogen blanket. The solid was dried *in vacuo* for about 24 hr.

The complexes are soluble in polar organic solvents such as acetone, nitromethane, methanol, and acetonitrile but are insoluble in nonpolar solvents such as carbon tetrachloride, benzene, hydrocarbons, and ether. The complexes are also soluble in water but decompose immediately to the hydrated metal perchlorates. They are stable in air and are not hygroscopic.

Analytical data for the complexes are presented in Table I.

TABLE I

ANALYTICAL DATA FOR NIPA COMPLEXES[a]

Compound	% carbon Calcd	% carbon Found	% hydrogen Calcd	% hydrogen Found	% nitrogen Calcd	% nitrogen Found	Color
$MgL_3(ClO_4)_2$	28.9	28.9	7.28	7.18	18.7	18.2	White
$CaL_3(ClO_4)_2$	28.5	28.3	7.18	7.02	18.5	17.7	White
$SrL_3(ClO_4)_2$	27.4	27.6	6.89	7.02	17.7	17.3	White
$BaL_3(ClO_4)_2$	26.3	25.6	6.61	6.58	17.0	16.6	White
$AlL_3(ClO_4)_3$	26.5	26.6	6.68	6.70	17.2	16.6	White
$MnL_3(ClO_4)_2$	28.2	27.8	7.09	7.01	18.2	17.9	White
$FeL_3(ClO_4)_3$	25.9	26.0	6.52	6.69	16.8	16.7	Yellow
$CoL_3(ClO_4)_2$	28.1	27.9	7.06	6.90	18.2	18.0	Pink
$NiL_3(ClO_4)_2$	28.1	27.8	7.06	7.02	18.2	17.8	Yellow
$CuL_2(ClO_4)_2$	25.1	25.4	6.31	6.47	16.3	16.4	Pale blue
$CuL_3(ClO_4)_2$	28.0	27.8	7.04	7.10	18.1	17.9	White
$ZnL_3(ClO_4)_2$	27.9	27.8	7.03	7.05	18.1	18.2	White
$HgL_3(ClO_4)_2$	25.0	25.0	6.29	5.99	16.2	15.9	White
$ThL_4(ClO_4)_4$	23.7	23.5	5.96	5.94	15.3	14.9	White
$UO_2L_3(ClO_4)_2$	23.9	23.3	6.02	5.93	15.5	14.9	Yellow

[a] Elemental analyses were done by Galbraith Laboratories, Knoxville, Tenn.

Conductance Measurements.—A conductance bridge manufactured by Industrial Instruments, Inc., was used to measure the conductivities of the complexes in nitromethane solutions. A platinum dip-type cell with a cell constant of 0.11 was used. The conductance data are summarized in Table II.

TABLE II

INFRARED SPECTRAL AND CONDUCTANCE DATA FOR NIPA COMPLEXES

Compound	ν-(P=O), cm^{-1}	ν-(PNP), cm^{-1}	ν-(PNC), cm^{-1}	ν-(PNC), cm^{-1}	Λ_{molar}, cm^2 ohm^{-1} mol^{-1}	Concn $\times 10^3$, *M*
NIPA	1195	885	978	745		
$MgL_3(ClO_4)_2$[a]	1215 s 1179 w 1161 m	900	980 990	746	190	1.01
$CaL_3(ClO_4)_2$	1209 s 1195 m 1160 w	895	990 978	749	191	1.02
$SrL_3(ClO_4)_2$	1185 s 1155 sh	885	989	751	187	1.04
$BaL_3(ClO_4)_2$	1182 1155 sh	880	988	749	194	1.00
$AlL_3(ClO_4)_3$	1170	900	993	760	264	1.04
$MnL_3(ClO_4)_2$	1202 s 1161 m	900	980 990	750	181	1.02
$FeL_3(ClO_4)_3$	1168 s	889	995	760	253	0.99
$CoL_3(ClO_4)_2$	1201 s 1160 m	900	980 990	749	180	1.01
$NiL_3(ClO_4)_2$	1203 s 1162 m	900	981 991	749	177	1.01
$CuL_2(ClO_4)_2$	1155 s	892	1005 990	758	179	1.30
$CuL_3(ClO_4)_2$	1202 s 1165 m	902	991 983	750	190	1.02
$ZnL_3(ClO_4)_2$	1204 s 1162 m	901	980 990	748	185	1.00
$HgL_3(ClO_4)_2$	1180 m 1141 m	885	989	751	188	1.03
$ThL_4(ClO_4)_4$[b]	1172	891	995	758	286	1.00
$UO_2L_3(ClO_4)_2$	Broad		985	753	164	1.03

[a] s, strong; m, medium; w, weak; sh, shoulder. [b] KBr pellet.

Spectral Measurements.—Infrared spectra were obtained for Nujol mulls of the complexes with a Beckman IR-10 spectrophotometer. The ir data are summarized in Table II. Near-infrared, visible, and ultraviolet spectra were obtained with a Beckman DK-2A spectrophotometer.

Calculation of *Dq* and $\beta°$.—The *Dq* and $\beta°$ parameters were calculated by the standard procedure.[7] The *Dq* value of NIPA

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[7] R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1965, pp 410, 411.

toward Ni(II) is 727 cm^{-1} ($10Dq$ = 7273 cm^{-1}). The value calculated for the P–F term splitting is 14,300 cm^{-1} and $\beta°$ is 9.7%. The calculated frequency of the middle peak is 12,300 cm^{-1} and the experimental value is 12,407 cm^{-1}. These spectral data are in support of octahedral Ni(II) in acetone solution.

Results and Discussion

The complexes of nonamethylimidodiphosphoramide are very similar in appearance and properties to the corresponding octamethylpyrophosphoramide complexes. This is to be expected since the only difference between the two ligands is the substitution of an N-methyl group for the bridging oxygen in OMPA.

For solutions of electrolytes in nitromethane, molar conductance values are usually in the range 15–20 cm^2 ohm^{-1} mol^{-1} or less for nonelectrolytes, 80–90 cm^2 ohm^{-1} mol^{-1} for 1:1 electrolytes, 130–180 cm^2 ohm^{-1} mol^{-1} for 2:1 electrolytes, and 200–250 cm^2 ohm^{-1} mol^{-1} for 3:1 electrolytes.[8] The values found for the NIPA complexes (Table II) are slightly higher than these ranges but are in agreement with those obtained for the corresponding OMPA complexes.[3] Molar conductance values were measured over the 10^{-2}–10^{-4} M concentration range in nitromethane for NIPA complexes of Sr(II), Mn(II), Fe(III), and Al(III) perchlorates. The relative difference in the molar conductance values for 2:1 and 3:1 electrolytes was maintained over the 10^{-2}–10^{-4} M concentration range with all molar conductance values increasing with dilution, as expected. Therefore, no special association effects or solvolysis reactions seem to be present. Although no range of values was given for 4:1 electrolytes, the values of 315 and 286 cm^2 ohm^{-1} mol^{-1} obtained for Th(OMPA)$_4$(ClO$_4$)$_4$ and Th(NIPA)$_4$(ClO$_4$)$_4$, respectively, seem reasonable.

The visible and near-infrared spectrum of the Ni(II) complex in acetone solution consists of three low-intensity peaks at 420 (ϵ 17), 806 (ϵ 6), and 1375 mμ (ϵ 5). The Nujol mull spectrum of the Ni(II) complex was obtained by using the technique reported by Lee, Griswold, and Kleinberg.[9] A peak was observed at 418 mμ which is in good agreement with the 420-mμ peak obtained in acetone. Peaks corresponding to those observed at 806 and 1375 mμ in acetone are apparently too weak to be observed by the mull technique.

The acetone spectrum is typical of octahedral Ni(II) and the peaks at 420, 806, and 1375 mμ can be assigned to the electronic transitions $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{2g}$, respectively. The $^3A_{2g} \rightarrow {}^3T_{2g}$ transition is equal to $10Dq$ in the octahedral configuration, and for Ni(NIPA)$_3$(ClO$_4$)$_2$ this is 7273 cm^{-1}. The Dq value of NIPA (727 cm^{-1}) is the same as that of OMPA (726 cm^{-1}).[10] This places NIPA at the lower end of the spectrochemical series. The $\beta°$ value for NIPA is 9.7% compared to 11.2% for OMPA.[10] Thus NIPA is also at the lower end of the nephelauxetic series.

The spectrum of Co(NIPA)$_3$(ClO$_4$)$_2$ in acetone indicates the presence of octahedrally coordinated Co(II). The visible spectrum has one low-intensity peak at 542 mμ (ϵ 25). The peak is asymmetric which can be attributed to an unresolved peak at about 500 mμ. The Nujol mull spectrum of the Co(II) complex has a peak at 538 mμ. The similarity of the mull and solution spectrum is evidence that no change in species occurs when the complex is dissolved in acetone.

Walmsley and Tyree[11] observed a peak at 538 mμ with a shoulder at 467 mμ for Co(L)$_3$(ClO$_4$)$_2$ where L = (C$_3$H$_7$O)$_2$P(O)CH$_2$P(O)(OC$_3$H$_7$)$_2$. The peak at 538 mμ was attributed to the transition $^4T_{1g} \rightarrow {}^4A_{2g}(F)$, and the peak at 476 m$\mu$ to the transition $^4T_{1g} \rightarrow {}^4T_{1g}(P)$. The peaks for Co(NIPA)$_3$(ClO$_4$)$_2$ which correspond to these transitions are at 542 and 500 mμ.

Since the coordinating ability of NIPA is similar to that of OMPA, we were interested in the possibility of isolating a tris chelate of Cu(II) with NIPA. When the same conditions as those for the preparation of Cu(OMPA)$_3$(ClO$_4$)$_2$ are used, only Cu(NIPA)$_2$(ClO$_4$)$_2$ is obtained.[12] However, by altering the procedure (see Experimental Section) it is possible to isolate Cu(NIPA)$_3$(ClO$_4$)$_2$. Since the color of the bis complex of Cu(II) with NIPA is pale blue while the tris complex is colorless, we decided to examine the electronic spectra of these complexes.

The spectra of both Cu(NIPA)$_2$(ClO$_4$)$_2$ and Cu(NIPA)$_3$(ClO$_4$)$_2$ in acetonitrile give a charge-transfer peak at 281 mμ (ϵ 1600). The spectrum of Cu(NIPA)$_2$(ClO$_4$)$_2$ in nitromethane gives an asymmetric peak with a maximum at 815 mμ (ϵ 43). This type of spectrum is characteristic of tetragonal Cu(II).[13] As excess NIPA is added to the bis complex, the spectrum changes as shown in Figure 1. Curve 2 in Figure 1 agrees with that obtained for the spectrum of Cu(NIPA)$_3$(ClO$_4$)$_2$ when enough extra NIPA has been added to make the total ratio of ligand to metal 4:1. When a large excess of NIPA is added, the peak appears to begin to resolve into three or four peaks. Addition of more NIPA results in a cloudy solution. The presence of the isosbestic points at 592 and 862 mμ indicates that the two major species present in solution are Cu(NIPA)$_2^{2+}$ and Cu(NIPA)$_3^{2+}$. The spectrum of Cu(NIPA)$_3$(ClO$_4$)$_2$ is quite similar to that of Cu(OMPA)$_3$(ClO$_4$)$_2$.[12] Thus we have the second example of a six-coordinate Cu(II) complex which has no absorption peaks in the visible region.

Infrared data are summarized in Table II. The PNP stretch has been assigned to the peak at 885 cm^{-1}. This assignment was arrived at by comparing the spectrum of hexamethylphosphoramide with octamethylpyrophosphoramide and nonamethylimidodiphosphoramide. The only difference in the spectra of these three compounds is the appearance of a peak for OMPA and NIPA at 885 and 915 cm^{-1}, respectively. Since the only difference in this series is the PNP and POP bridge, the peak at 885 cm^{-1} is assigned to the PNP stretching frequency. The peak at 915 cm^{-1} for OMPA was previously assigned to the

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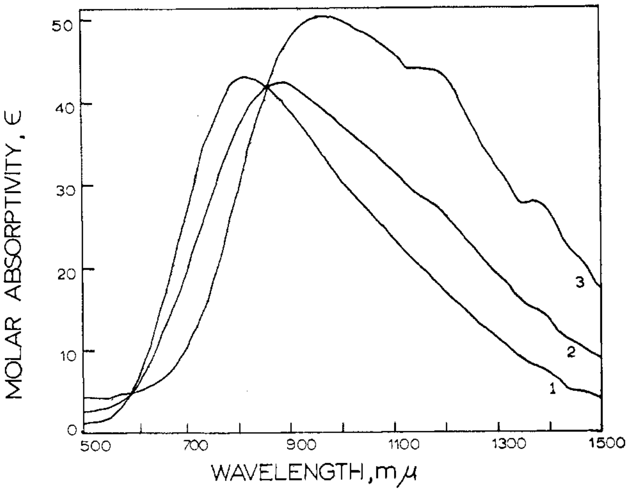

Figure 1.—Spectrum of $Cu(NIPA)_2(ClO_4)_2$ in nitromethane with varying amounts of excess ligand: (1) $Cu(NIPA)_2(ClO_4)_2$; (2) $Cu(NIPA)_2(ClO_4)_2$ + slight excess of NIPA; (3) $Cu(NIPA)_2(ClO_4)_2$ + large excess of NIPA.

POP stretching frequency.[14] Both the PNP and PNC stretching frequencies for complexes of NIPA are shifted to higher frequencies (Table II). The effect of coordination on the P=O stretching frequency is not easily interpreted. The peak assigned to the P=O stretch for the ligand is rather broad. In the complex this peak seems to be split into a sharp strong peak at ~1200 cm^{-1} and a sharp medium-intensity peak at ~1170 cm^{-1}. Walmsley and Tyree[11] reported splitting of the P=O stretching vibrations in some bidentate P=O ligands when more than one type of ligand was present in the inner coordination sphere. Cotton, Barnes, and Bannister[15] attributed P=O splitting or broadening to coupling between two P=O vibrations *via* the metal atom to which both are coordinated or to the existence of nonequivalent ligands in the crystal. Splitting was not usually present in perchlorate complexes. However, in $((C_6H_5)_3PO)_4Co(ClO_4)_2$ a sharp medium-intensity peak was observed at 1203 cm^{-1} and a strong peak at 1160 cm^{-1}. The peak at 1160 cm^{-1} was assigned to the P=O stretching vibration. No assignment was given for the peak at 1208 cm^{-1}.

The shifts in the PNP and PNC stretching frequencies may be explained similarly to those for the POP and PN stretching frequencies in OMPA.[14] The bond between the oxygen and the metal ion tends to withdraw electron density from the P=O bond and thus decrease the double-bond character. This results in a decrease in the P=O stretching frequency. Since electron density is drained from the P=O bond, there is a tendency for the lone pair on each of the nitrogen atoms to be delocalized into the available dπ orbitals of the phosphorus. The bond order between phosphorus and nitrogen would be expected to increase and this would cause an increase in the PNP and PNC stretching frequencies.

Chelation seems to be the important factor in stabilizing the complexes since stable complexes are formed in spite of the low positions of NIPA in the spectrochemical and nephelauxetic series. The substitution of the more electropositive N-methyl group for the bridge oxygen of OMPA has little influence on the stability of the complexes.

Acknowledgment.—Portions of this work were supported by USPHS Grant No. GM-15451-01.

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Effects of pH and Zinc Complex Formation on Phosphorus–Hydrogen Coupling Constants and Proton Chemical Shifts in Hypophosphorous and Phosphorous Acids

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The variation of J_{PH} with hydrogen ion concentration for solutions containing phosphite and hypophosphite species is shown to arise from rapid proton exchange among the various species present. Complex formation with zinc is shown to lead to similar increases in J_{PH}. The data are analyzed to give formation constants for mono- and bis(hypophosphito)zinc complexes.

Introduction

Two recent papers deal with variation with pH of phosphorus–hydrogen coupling constants and ^{31}P chemical shifts in phosphorous and hypophosphorous acid (among others). Moedritzer[2] studied the variation of the ^{31}P chemical shift and J_{PH} with degree of neutralization of the acids in aqueous solution. Sheldrick[3] studied the variation of J_{PH} in strongly acidic media—sulfuric acid from 12 to 98%.

The present paper is concerned with the origins of the variations in J_{PH} in terms of the chemical species in-

(1) NDEA Title IV Fellow.

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