

or at least improving yields of desirable products relative to those obtained under standard heterogeneous pyrolysis conditions. In preliminary experiments we have found that appropriate chopping can control $(BH)_n$ formation. On-off fast heating by laser pulsing or chopping and the subsequent effect upon convection flow patterns and reactant replenishment can lead to different quantitative results. Application of these effects to alter the reaction product distribution in synthesis is currently being investigated.

Acknowledgment. C.R. would like to express his gratitude to NSF for the Faculty Development Grant. C.R. also thanks the LIC group of the High Energy Laser Laboratory at Redstone Arsenal, Redstone, Ala., especially Drs. Richard Hartman and George Tanton, for their cooperation.

Registry No. B₂H₆, 19287-45-7; SF₆, 2551-62-4; B₃H₉, 19624-22-7; B₅H₁₁, 18433-84-6; B₁₀H₁₄, 17702-41-9.

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Phosphorus-31 NMR of Triphenylphosphine Oxide Complexes with Compounds of Silicon, Germanium, and Tin

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Received May 4, 1978

Phosphorus-31 NMR of equimolar mixtures of Ph₃PO and compounds of the main group 4 elements in toluene exhibits downfield coordination shifts from the free base. The data are interpreted in terms of the formation of adduct complexes in solution. Analysis of the concentration dependency of the chemical shift permits the determination of the formation constant of the 1:1 complex and the change in chemical shift upon complexation where the 1:1 complex is the predominant species in solution. Thus, $K(\text{Ph}_3\text{PO}:\text{Me}_3\text{SiCl}) = 60 \pm 5 \text{ M}^{-1}$, $\Delta_c = 7.8 \text{ ppm}$, and $K(\text{Ph}_3\text{PO}:\text{Me}_3\text{SnCl}) = 100 \pm 5 \text{ M}^{-1}$, $\Delta_c = 3.2 \text{ ppm}$, where $\Delta_c = \delta_{\text{complex}} - \delta_{\text{Ph}_3\text{PO}}$. More complicated data, observed for SiCl₄-Ph₃PO solutions, suggest multiple equilibria. Data analysis at very low concentration gives $K(\text{Ph}_3\text{PO}:\text{SiCl}_4) \approx 180 \text{ M}^{-1}$ with $\Delta_c \approx 16 \text{ ppm}$. Additionally, an effect of added MeCN on the chemical shift of Ph₃PO-Me₃SiCl solutions has been observed and interpreted in terms of a coordinate interaction between the nitrilic group and silicon.

Introduction

Tertiary phosphine oxides are known to be weak bases. It has been suggested that the weak donor character may be due to $d\pi-p\pi$ bonding¹ which reduces the electron density on oxygen. That these oxides interact with protic acids to give hydroxyphosphonium salts and that they behave as weak donor ligands to Lewis acids by coordination through oxygen attest to their basic properties.²⁻⁶ Many such complexes with strong acceptors have been isolated and exhibit a characteristic shift in the phosphoryl stretching (P→O) frequency. Similar complexes of SiCl₄ with Ph₃PO and (Me₂N)₃PO, which have been suggested as intermediates in chlorosilane-siloxane redistribution reactions,⁷ have been isolated as solids;^{4,8} however, the decrease in $\nu(\text{P}\rightarrow\text{O})$ observed for the complexes as a mull ($\sim 45 \text{ cm}^{-1}$) is not detected when the complexes are dissolved in either polar or nonpolar solvents.^{8,9} Furthermore, the UV spectrum of Ph₃PO remains unchanged in the presence of a chlorosilane. It has been suggested that the lack of an observable change in the solution spectra (IR or UV) results from either a lack of complexation, appreciable dissociation

of the complex, or a weak dative interaction giving rise to a shift too small to be detected.⁹

It has recently been shown by Grim et al. that ³¹P NMR is a sensitive probe for the detection of complexes in solutions containing mono- and bidentate phosphorus ligands coordinated to transition metals.^{10,11} In each case sizable increases in chemical shift ($\delta_{\text{obsd}} - \delta_{\text{ligand}}$) have been observed and interpreted in terms of inductive effects resulting from a decrease in the electron density at phosphorus owing to oxygen coordination. In this paper we will describe the detection of Ph₃PO complexes with various silanes, siloxanes, and stannanes and tetrachlorogermane in solution by ³¹P NMR. Importantly, analysis of concentration-dependent ³¹P NMR chemical shifts provides a facile method for the determination of the formation constant for 1:1 addition complexes.

Experimental Section

Toluene and MeCN (Fisher Scientific, reagent grade) were purified by distillation under anhydrous conditions. Ph₃PO (Eastman Kodak, reagent grade) was purified by recrystallization from acetone. SiCl₄ (Fisher Scientific, reagent grade), Me₃SiCl, Me₂SiCl₂, and MeSiCl₃ were purified by distillation. Cl₃Si(OSiMe₂)₃Cl was prepared according to methods described earlier.⁷ The stannanes (Alfa Inorganics) were purified by recrystallization for solids and by distillation for liquids. All other chemicals were reagent grade and used without

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[†]In partial fulfillment of the requirements for the Ph.D. degree in Chemistry at the Polytechnic Institute of New York.

Table I. ^{31}P Chemical Shift Data of Equimolar (0.100 M) Solutions of Ph_3PO with Silanes, Siloxanes, Tetrachlorostannane, and Tetrachlorogermane in Toluene at 25°C

solution	δ , ppm	Δ , ^a ppm
Ph_3PO (1)	23.2	
(1) + Me_3Si (2)	23.2	0.0
(1) + Me_3SiBr (3)	23.3	0.1 ^b
(1) + Me_3SiCN (4)	23.7	0.5 ^b
(1) + Me_3SiOMe (5)	23.3	0.1 ^b
(1) + $(\text{Me}_2\text{SiO})_3$ (6)	25.0 ^c	-0.2
(1) + SiCl_4 (7)	27.1	3.9
(1) + MeSiCl_3 (8)	25.4	2.2
(1) + Me_2SiCl_2 (9)	26.6	3.4
(1) + Me_3SiCl (10)	28.4	5.1
(1) + HSiCl_3 (11)	26.4	3.2
(1) + EtSiCl_3 (12)	25.6	2.4
(1) + PhSiCl_2 (13)	26.9	3.7
(1) + $(\text{ClMe}_2\text{SiO})_2\text{SiMe}_2$ (14)	26.8	3.6
(1) + $\text{Cl}_2\text{Si}(\text{OSiMe}_2)_2\text{Cl}$ (15)	27.1	3.9
(1) + GeCl_4 (16)	26.9	3.7
(1) + SnCl_4 (17)	37.7	14.5 ^d
(1) + Me_2SnCl_2 (18)	29.2	5.6
(1) + Et_2SnCl_2 (19)	27.0	4.6
(1) + Me_3SnCl (20)	25.5	2.3
(1) + Me_3SiCl + MeCN (0.07) ^e	31.4	8.2
(1) + Me_3SiCl + MeCN (0.33) ^e	32.8	9.6

^a $\Delta = \delta - \delta_f$. ^b Δ varies by ± 0.2 ppm with a mole ratio ($\text{Ph}_3\text{PO}:\text{Me}_3\text{SiX}$) from 1:10. ^c Data taken in a mixed solvent of toluene (90%)-acetonitrile (10%). ^d Δ varies by ± 0.1 ppm over a concentration range from 0.1 to 0.025 M. ^e Volume fraction.

Table II. Concentration-Dependent ^{31}P Chemical Shift Data for Equimolar Solutions of Ph_3PO and Me_3SiCl in Toluene at 25°C

$[\text{Ph}_3\text{PO}] =$ $[\text{Me}_3\text{SiCl}]$	Δ , ^a ppm		$(\Delta/C_0)^{1/2}$, (ppm $\text{M}^{-1})^{1/2}$	
	I	II	I	II
0.100	5.1	5.4	7.1	7.3
0.067	4.7	4.9	8.3	8.5
0.050	4.3	4.5	9.3	9.5
0.033	4.0	4.1	11	11
0.025	3.5	3.7	12	12

^a $\Delta = \delta - \delta_f$.

Table III. Concentration-Dependent ^{31}P Chemical Shift Data for Equimolar Solutions of Ph_3PO and Me_3SnCl in Toluene at 25°C

$[\text{Ph}_3\text{PO}] =$ $[\text{Me}_3\text{SnCl}]$	Δ , ^a ppm	$(\Delta/C_0)^{1/2}$, (ppm $\text{M}^{-1})^{1/2}$
0.075	2.2	5.4
0.067	2.1	5.6
0.050	2.0	6.3
0.033	1.8	7.4
0.025	1.7	8.2

^a $\Delta = \delta - \delta_f$.

further purification. All solutions were prepared under anhydrous conditions. ^{31}P NMR data were collected at 36.43 MHz on a Bruker HFX-90 spectrometer modified for multinuclear measurements as described by Traficante et al.¹² and equipped with a Digilab computer system. Samples were placed in 10-mm tubes and the ^{19}F lock signal was provided by C_6F_6 in a concentric 2-mm tube. Chemical shifts were measured relative to 85% H_3PO_4 where positive values correspond to the low-field side of the reference.

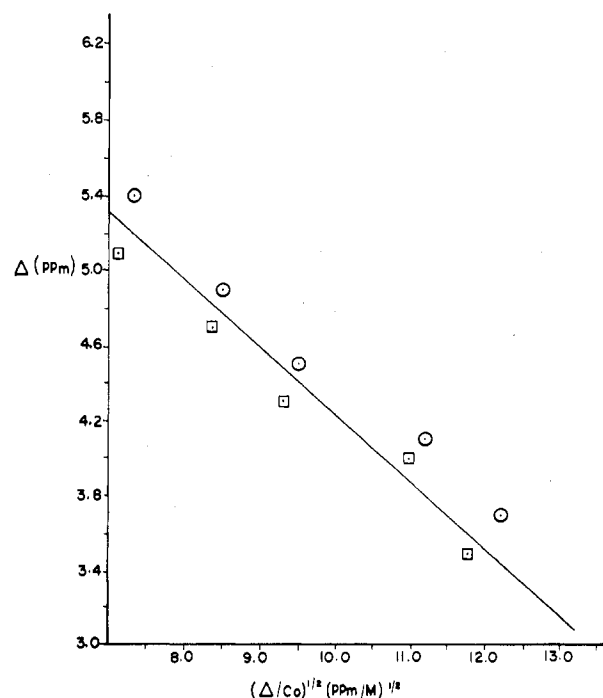
^{31}P NMR chemical shift data of the samples containing equimolar (0.100 M) concentrations of triphenylphosphine oxide and various silanes, siloxanes, and stannanes or tetrachlorogermane in toluene at 25°C are summarized in Table I. The concentration-dependent chemical shift data of Me_3SiCl , Me_3SnCl , and SiCl_4 with Ph_3PO are given in Tables II-IV. The chemical shift of Ph_3PO in toluene on addition of MeCN has been determined (Δ , ppm (volume fraction)): -0.1 (0.02), 0.3 (0.06), 0.1 (0.15).

The evaluation of the formation constant for a 1:1 complex (D:A) between a donor (D) and an acceptor (A) from ^{31}P chemical shift

Table IV. Concentration-Dependent ^{31}P Chemical Shift Data for Equimolar Solutions Containing Ph_3PO and SiCl_4 in Toluene at 25°C

$[\text{Ph}_3\text{PO}] =$ $[\text{SiCl}_4]$	Δ , ^a ppm		$(\Delta/C_0)^{1/2}$, (ppm $\text{M}^{-1})^{1/2}$	
	I	II	I	II
0.100	3.9		6.3	
0.075	4.4		7.7	
0.050	4.7		9.7	
0.025	4.8		13.9	
0.0050	5.9	5.9	34	34
0.0043	5.2	5.2	35	35
0.0038	5.0	5.1	36	37
0.0033	4.5	4.7	37	38

^a $\Delta = \delta - \delta_f$.

**Figure 1.** Plot of Δ vs. $(\Delta/C_0)^{1/2}$ for $\text{Ph}_3\text{PO}-\text{Me}_3\text{SiCl}$ solutions from 0.100 to 0.025 M: (\square) experiment I, (\circ) experiment II.

data of equimolar solutions of the reagents may be carried out using a modified form of eq 1 derived by Drago¹³ where Δ is the difference

$$K = \Delta / ((\Delta_c - \Delta)[D]_0 - \Delta[A]_0 / \Delta_c) \quad (1)$$

between the chemical shift of the solution (δ) and that of the free ligand D (δ_f), Δ_c is the difference between the chemical shift of the complex D:A (δ_c) and the free base, and $[D]_0$ and $[A]_0$ are the initial concentrations of D and A. For the case where $[D]_0 = [A]_0 = C_0$, eq 1 can be rearranged to eq 2. Since Δ_c is a constant, a plot of Δ

$$\Delta = \Delta_c - (\Delta_c/K)^{1/2}(\Delta/C_0)^{1/2} \quad (2)$$

vs. $(\Delta/C_0)^{1/2}$ should be linear with slope $-(\Delta_c/K)^{1/2}$ and intercept Δ_c . K can be calculated from the slope and intercept: $K(\text{Ph}_3\text{PO}:\text{Me}_3\text{SiCl}) = 60 \pm 5 \text{ M}^{-1}$ (Table II, Figure 1), $K(\text{Ph}_3\text{PO}:\text{Me}_3\text{SnCl}) = 100 \pm 5 \text{ M}^{-1}$ (Table III, Figure 2), $K(\text{Ph}_3\text{PO}:\text{SiCl}_4) = 180 \pm 10 \text{ M}^{-1}$ (Table IV, Figure 3).

Results and Discussion

With the exception of non-chlorine-containing silicon compounds (2-6), the ^{31}P NMR data (Table I) of toluene solutions containing equimolar amounts of Ph_3PO (1) and various compounds of the main group 4 elements exhibit a significant downfield coordination shift, $\Delta(\delta - \delta_f)$, from the free base. The magnitudes of the shifts (2.2-5.6 ppm) for chlorosilanes (7-13), chlorodimethylsiloxanes (14,15), tetrachlorogermane (16), and organochlorostannanes (18-20) suggest that the dative interaction between the phosphoryl

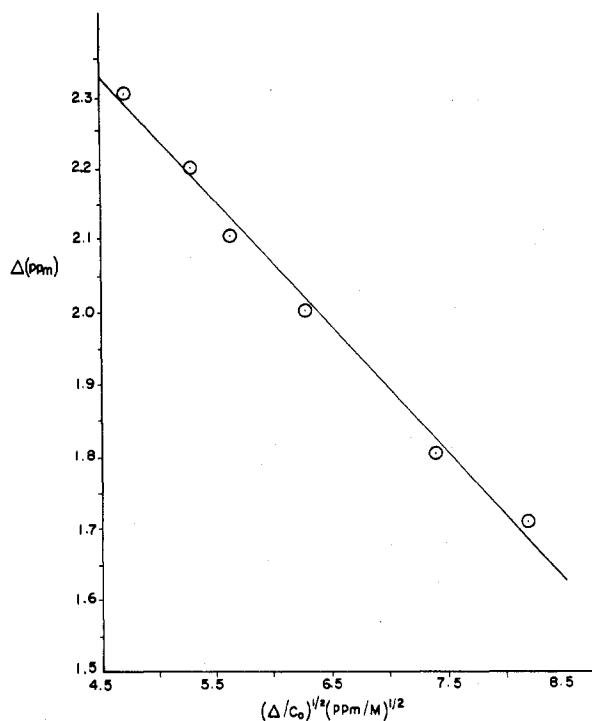


Figure 2. Plot of Δ vs. $(\Delta/C_0)^{1/2}$ for $\text{Ph}_3\text{PO-Me}_3\text{SnCl}$ solutions from 0.100 to 0.025 M.

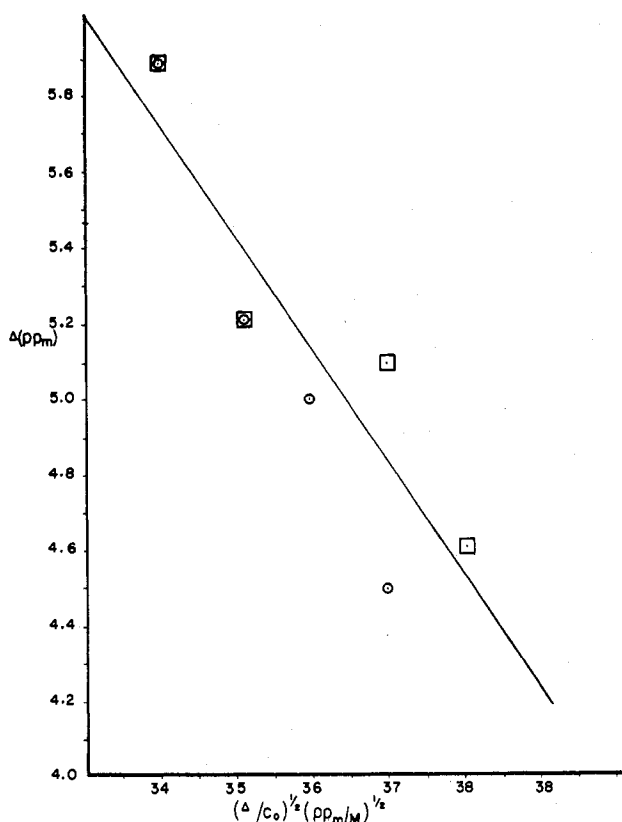


Figure 3. Plot of Δ vs. $(\Delta/C_0)^{1/2}$ for $\text{Ph}_3\text{PO-SiCl}_4$ solutions from 0.0050 to 0.0033 M: (□) experiment I, (○) experiment II.

oxygen and the metal results in a molecular adduct analogous to certain phosphine oxide complexes of zinc, cadmium, and mercury (viz., $(\text{Ph}_3\text{PO})_2\text{HgBr}_2$, $\Delta = 5.8$ ppm; $[(\text{Ph}_2\text{P}(\text{O}))_2\text{CH}_2]\text{MCl}_2$, $\Delta_{\text{Zn}} = 5.4$ ppm, $\Delta_{\text{Cd}} = 5.0$ ppm).^{10,11} This is in sharp contrast to Δ values which exceed 20 ppm for phosphine oxide ligands bonded to metals in an ionic environment or protonated with strong acids (viz., $[(n-$

$\text{Bu}_3\text{PO})_4\text{Zn}](\text{ClO}_4)_2$, $\Delta = 25.7$ ppm;¹⁰ $\text{Ph}_3\text{POH}^+\text{X}^-$, $\Delta_{\text{Cl}} = 21.5$ ppm,^{9,14} $\Delta_{\text{Br}} = 27.3$ ppm¹⁵). It is noteworthy that a 0.1 M solution of Ph_3PO and SnCl_4 (17) has a relatively large Δ (14.5 ppm) which indicates either considerable polar character in the dative bond or the presence of an ionic complex, e.g., $[(\text{Ph}_3\text{PO})_x\text{SnCl}_3]^+\text{Cl}^-$, $x = 1, 2$. The high solubility of the complex in nonpolar solvents such as toluene or pentane precludes the latter formulation. Since Δ values for complexes of Ph_3PO with alkylchlorostannanes (18–20) and organochlorosilanes (8–15) are relatively small and concentration dependent, it is reasonable to conclude that solution shifts alone cannot be used to deduce the nature of electronic or steric factors.

It has been observed that no significant coordination shift occurs for solutions of Ph_3PO and 2–6 even if the acceptor is present in large excess. Perhaps this is expected since it is well documented that silicon in compounds containing one or more such groups (Br, OR, CN) are, at best, very weak acceptors even toward stronger bases such as trialkylamines^{16–18} (one class of exceptions is the silatranes¹⁹). This is not the case for chlorosilanes where a downfield coordination shift is detected for a wide variety of substituents (e.g., H, Me, Et, Ph, MeO, Me_2SiO , Me_3SiO).

For all of the chlorosilanes and chlorostannanes examined in the present study, Δ is concentration dependent. It is believed that the dependency is a result of a rapid exchange between the free and complexed ligand giving rise to an observed chemical shift which is a weighted average of the ligand in both environments. If a 1:1 complex predominates in solution, eq 2 can be used to determine both the formation constant and the chemical shift of the complex from concentration-dependent data. Results for $\text{Ph}_3\text{PO-Me}_3\text{SiCl}$ and $\text{Ph}_3\text{PO-Me}_3\text{SnCl}$ solutions in a concentration range from 0.100 to 0.025 M are summarized in Tables II and III, respectively. Figures 1 and 2 represent plots of Δ vs. $(\Delta/C_0)^{1/2}$ for the silicon and tin solutions, respectively. The linearity of the plot confirms the molecularity of the complex. From the slope and intercept, the formation constant and Δ for the 1:1 complexes have been calculated ($K_{\text{Si}} = 60 \pm 5 \text{ M}^{-1}$, $\Delta_c = 7.8$ ppm; $K_{\text{Sn}} = 100 \pm 5 \text{ M}^{-1}$, $\Delta_c = 3.2$ ppm).

Comparable studies with SiCl_4 , which is a known mono- and bifunctional acceptor toward stronger bases,^{8,19} give more complicated data (Table IV). Above 5×10^{-3} M, Δ decreases with increase in concentration. It is believed that the variation in the direction of chemical shift as a function of concentration is a result of the formation of at least two complexes ($\text{Ph}_3\text{PO}:\text{SiCl}_4$ and $2\text{Ph}_3\text{PO}:\text{SiCl}_4$) in solution with the possibility of several isomeric forms for each complex. Interestingly, $2\text{Ph}_3\text{PO}:\text{SiCl}_4$ has been isolated and characterized as a solid;⁴ however, neither the 1:1 nor the 2:1 complex has been detected in solution by IR, UV, or ¹H NMR techniques.⁹ For very dilute solutions ($<5 \times 10^{-3}$ M) eq 2 appears to be applicable. Analysis of these data in terms of predominance of the 1:1 complex yields a formation constant of approximately 180 M^{-1} with $\Delta_c \approx 16$ ppm.

The above data represent the first report of the determination of formation constants in solution for complexes of chlorosilanes. Previously, Burg²⁰ described solid complexes of SiCl_4 , HSiCl_3 , and H_2SiCl_2 with the stronger base Me_3N . With SiCl_4 , the complex was stable only at low temperatures with a formation constant of 560 M^{-2} estimated from dissociation pressure data. One cannot compare this formation constant value with those obtained in the present study owing to differences in base, phase, and temperature. However, it is clear from the solution studies that stannane complexes are slightly more stable than silane complexes as might be expected from the relative differences in acceptor ability of the metal. Moreover, the slightly larger formation constant for the

complex $(\text{Me}_2\text{N})_3\text{PO}:\text{Me}_3\text{SnCl}$ ($K = 380 \text{ M}^{-1}$ in isooctane at 26°C^{21}) determined by ^1H NMR is consistent with the stronger donor characteristics of the phosphoramidate base.

Chlorosilanes and chlorostannanes containing more than one chlorine exhibit complicated, concentration-dependent coordination shifts analogous to the behavior of SiCl_4 , presumably due to the presence of several complexes along with the possibility of isomeric forms.²² Further studies designed to determine K_2 values are currently under way.

It is worthwhile to note the substantial effect of added acetonitrile on the chemical shift of the $\text{Ph}_3\text{PO}:\text{Me}_3\text{SiCl}$ complex (Table I). Downfield resonance shifts exceed 3 ppm even with low concentrations (7% by volume) of MeCN. Since MeCN does not affect the chemical shift of Ph_3PO , the magnitude of the solvent-induced shift of the complex cannot be attributed solely to changes in the bulk susceptibility of the solvent. Some argument can be made for a shift due to magnetic anisotropy of the nitrilic moiety. Upon complexation with the metal, the highly polarized phosphoryl group may interact with the polarizable π electrons of MeCN thus inducing a shift owing to a nonzero orientational averaging of MeCN in proximity to the complex. Alternatively, acetonitrile may coordinate to phosphorus or, more likely, to silicon or tin, thus expanding the element's coordination number to 6. It appears that Δ increases upon further addition of the solvent, which suggests that the adduct is trimolecular ($\text{Ph}_3\text{PO}:\text{Me}_3\text{SiCl}:\text{MeCN}$). If indeed, coordination is to silicon, then these observations represent the first direct evidence for such a complex. Further quantitative investigations are currently being carried out to resolve this point.

Acknowledgment. The authors gratefully acknowledge the helpful suggestions and discussions with Professor Herbert Morawetz and Dr. D. H. Marr. We also thank Mr. J. A. Mylie for his technical assistance in carrying out some of the NMR experiments.

Registry No. 1, 791-28-6; 1-7, 68307-43-7; 1-8, 68307-44-8; 1-9, 68332-32-1; 1-10, 68307-45-9; 1-11, 68307-46-0; 1-12, 68307-47-1; 1-13, 68307-48-2; 1-14, 68307-49-3; 1-15, 68307-50-6; 1-16, 68307-51-7; 1-17, 28176-41-2; 1-18, 68307-52-8; 1-19, 61646-57-9; 1-20, 23209-03-2; $\text{Ph}_3\text{PO}:\text{Me}_3\text{SiCl}:\text{MeCN}$, 68307-53-9.

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Far-Infrared Spectra of Ammonium, Potassium, Rubidium, and Cesium Metavanadates

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Received July 13, 1978

The far-infrared spectra of NH_4VO_3 , ND_4VO_3 , KVO_3 , RbVO_3 , and CsVO_3 have been measured at room and low temperatures. The VO_2 and VOV bending vibrations were assigned to the bands in the regions $390\text{--}330$ and $280\text{--}210 \text{ cm}^{-1}$, respectively. A linear relationship between the cation translations of these salts and $m^{-1/2}$ (m = mass of the cation) led to the suggestion that these salts have similar force constants for the translational modes. Temperature dependence of the librational absorption of the ammonium ion has also been discussed. The potential barrier of the restricted rotation was estimated to be 5.0 kcal/mol .

The crystals of metavanadates, MVO_3 ($\text{M} = \text{NH}_4, \text{K}, \text{Rb}, \text{and Cs}$), have a peculiar structure in which the tetrahedral VO_4 groups constitute a chain arrangement.¹ The space group is $Pmab\text{-}D_{2h}^{11}$ and the unit cell contains four molecules including four equivalent cations. Few vibrational studies for these crystals are found in the literature.² It is interesting for NH_4VO_3 that two librational bands of the NH_4^+ ion were found by the measurements of neutron scattering³ while the four NH_4^+ ions are located at the equivalent sites in a cell. These two bands have been interpreted as arising from two- and threefold librational modes on the basis of the NMR relaxation times.⁴

In order to investigate the motions of the ions in metavanadates, far-infrared spectra of NH_4VO_3 , ND_4VO_3 , KVO_3 ,

RbVO_3 , and CsVO_3 powders were measured at room and low temperatures. This paper reports the assignments for the low-frequency absorptions with some discussions.

Experimental Section

Materials. NH_4VO_3 and KVO_3 were commercially obtained. ND_4VO_3 was obtained as the precipitate by the reaction $\text{NaVO}_3 + \text{ND}_4\text{Cl} \rightarrow \text{ND}_4\text{VO}_3 + \text{NaCl}$ (in D_2O). This powder showed a little absorption of the NH stretching due to the impurity. RbVO_3 (mp 673°C) and CsVO_3 (mp 755°C) were prepared, respectively, by the following reactions: $\text{Rb}_2\text{CO}_3 + \text{V}_2\text{O}_5 \rightarrow 2\text{RbVO}_3 + \text{CO}_2$ and $\text{Cs}_2\text{CO}_3 + \text{V}_2\text{O}_5 \rightarrow 2\text{CsVO}_3 + \text{CO}_2$.

Measurements. A Hitachi FIS-1 far-infrared spectrophotometer was used to record the spectra. Each salt was milled with paraffin wax on a 0.5 mm thick polyethylene sheet. Low-temperature spectra