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Addition Compounds of Phosphorus(V) Chloride and Aromatic Nitrogen Bases. Crystal Structure and ^{1}H NMR and Raman Spectra of Pyrazine–Phosphorus(V) Chloride

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The solid-state structure of a nonionic adduct of phosphorus(V) chloride and pyrazine, $C_4H_4N_2{\cdot}PCl_5$, shows phosphorus to be six-coordinate with one octahedral position occupied by a nitrogen atom of the pyrazine ring. The monoclinic crystal is of space group $C2/c$ having four molecules per unit cell of dimensions a = 8.359 (8) Å, b = 16.202 (15) Å, c = 7.568 (7) Å, and β = 99.37 (7)°. The structure was refined by least squares to R = 0.097 by using 1754 independent reflections collected to $2\theta_{max}$ = 65° and corrected for absorption. The P–N distance is 2.021 (5) Å. In nitromethane solution, Raman, ^{1}H NMR, cryoscopic, and conductivity measurements are interpreted in terms of equilibria involving $C_4H_4N_2{\cdot}PCl_5$, pyrazine, molecular PCl_5, and ions originating from the ionization of PCl_5 and $C_4H_4N_2{\cdot}PCl_5$.

Introduction

A review of the literature reveals that most structural information regarding nonionic adducts of PCl_5 has been obtained from vibrational spectra and NMR or is implied from stoichiometry. Crystallographic data on neutral six-coordinate adducts of phosphorus pentachloride appear to be altogether missing from the literature, although several crystal structures are to be found involving PCl_4^+ associated with a variety of chloride acceptors. Specifically, the structure of a complex between PCl_5 and ICl contains PCl_4^+ and ICl_2^- ions,[1] while PCl_5 and $TeCl_4$ react to form PCl_4^+ and a polymeric chain anion based on a distorted $TeCl_6$ octahedron.[2] In addition, Preiss' X-ray data on the reaction products between PCl_5 and $NbCl_5$ and between PCl_5 and $TaCl_5$ yield PCl_4^+ tetrahedra and MCl_6^- octahedra.[3] A 1:1 addition of PCl_5 to UCl_5 has been shown by Raman spectroscopy to contain PCl_4^+ and UCl_6^- ions.[4]

For py·PCl_5 (py = pyridine) Holmes[5] proposes a molecular formulation based on molecular weight and conductance measurements in nitrobenzene. A tensimetric titration of PCl_5 with $(CH_3)_3P$ in bromobenzene solution gives a white solid of composition $(CH_3)_3P_{1.97}PCl_5$, but no structural assignment has been made.[6] Chadha[7] reports on the other hand that 1:1 adducts between PCl_5 and pyridine, β- and γ-picoline, quinoline, isoquinoline, and piperidine are all univalent electrolytes in nitrobenzene. Beattie[8] has measured the vibrational spectrum of py·PCl_5 in the solid state and concludes that the adduct is molecular. The extensive ^{31}P NMR study of pyridine and substituted pyridine bases by Dillon, Reeve, and Waddington[9-11] concurs that the adducts are molecular octahedra. Pyridine, pyrazine, and 3-substituted pyridines appear to be completely associated with PCl_5 in solutions of high base concentration. Partial association was found for 3,5-dichloropyridine (60% associated), whereas the 2-chloro and 2-fluoro derivatives undergo very little association with PCl_5 in nitrobenzene.

Muetterties[12] has reported ^{19}F NMR spectra on a series of adducts with PF_5 wherein two sets of doublets and quintets provide evidence for four equatorial and one axial fluorine atoms. In solution these compounds are formulated as six-coordinate octahedra with one site occupied by a Lewis base. Sheldrick's X-ray structure of the pyridine adduct of PF_5 verifies the octahedral coordination.[13] The P–N bond distance is 1.885 (4) Å.

Earlier we reported the synthesis and solution behavior of a pyrazine (pyz)–phosphorus(V) chloride adduct.[14] ^{1}H NMR in nitromethane solution showed equivalence of protons on the pyrazine ring. Evidence for a bound vs. free pyrazine exchange which could not be slowed for NMR observation at −100 °C was cited. An apparent molecular weight equal to half of the formula weight was obtained by freezing point measurements, while conductivity measurements indicated ions in solution.

We address in this paper the subject of the solid-state structure, the solution structure, and solution equilibria of the adduct pyz·PCl_5 by means of X-ray crystallography, laser Raman, and ^{1}H NMR studies.

Experimental Section

Crystallographic Analysis. pyz·PCl_5 was prepared as previously described.[14] Several 0.5-mm glass capillary tubes were filled with powdered samples of the complex in a drybox to a depth of 5 mm. The tubes were sealed with a torch, and the material was sublimed in an oil bath at 74 °C. Periodic inspection of the tubes revealed a suitable single crystal, 0.35 mm × 0.25 mm × 0.01 mm, in one of the tubes after 4 days of heating.

The density was estimated to be in the range 1.59–1.96 g/cm^3 by noting the behavior of the crystals in CCl_4 and *o*-dibromobenzene. The calculated density is 1.89 g/cm^3 on the basis of Z = 4 and the molecular weight of 288.[14]

The crystal is monoclinic of space group $C2/c$, with unit cell dimensions of a = 8.359 (8) Å, b = 16.202 (15) Å, c = 7.568 (7) Å, β = 99.37 (7)°, and V = 1011 Å^3. Precise lattice constants were calculated from the setting angles of 8 Friedel pairs having $34° < 2\theta$ (Mo Kα) $< 45°$.

The intensity data were collected at about 22 °C on a Picker FACS I diffractometer equipped with auxiliary disk memory and the Vanderbilt operating system.[15] The θ–2θ scan mode was used to measure 2896 reflections, of which 1754 were unique, out to a maximum 2θ of 65°. Stationary backgrounds were measured at 0.5° above and below the respective Kα peak of base width of 1.0°. There was no detectable decrease in the intensities of three standard reflections during the 11 days of continuous data collection. In fact, the crystal has remained unchanged in the sealed capillary for over $1^1/_2$ years during collection of two data sets. Sixty-eight high-angle reflections were inaccessible due to the nature of the capillary mounting device. Intensities were corrected for absorption (μ = 15.2 cm^{-1}) by

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Table I. Positional and Thermal Parameters[a] ($Å^2 \times 10^3$) and Their Estimated Standard Deviations

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	0.0000	0.3412 (1)	0.2500	47 (1)	36 (1)	33 (1)	0	10 (1)	0
Cl1	0.0000	0.4701 (1)	0.2500	83 (1)	34 (1)	65 (1)	0	12 (1)	0
Cl2	0.0010 (2)	0.3356 (1)	0.5310 (2)	84 (1)	53 (1)	35 (1)	5.8 (6)	17 (1)	−3.5 (4)
Cl3	0.2576 (2)	0.3367 (1)	0.2975 (2)	46 (1)	57 (1)	72 (1)	−6.3 (5)	12 (1)	−0.9 (6)
N1	0.0000	0.2165 (3)	0.2500	44 (3)	35 (2)	44 (2)	0	15 (2)	0
N2	0.0000	0.0440 (4)	0.2500	79 (5)	38 (3)	108 (6)	0	30 (4)	0
C1	0.1002 (6)	0.1730 (3)	0.1613 (7)	55 (3)	48 (2)	58 (3)	4 (2)	24 (2)	−5 (2)
C2	0.0982 (8)	0.0872 (3)	0.1641 (10)	77 (4)	41 (2)	94 (5)	1 (2)	34 (3)	−10 (3)

atom	x	y	z	U	atom	x	y	z	U
H1	0.179 (8)	0.210 (4)	0.105 (8)	50 (18)	H2	0.162 (8)	0.060 (4)	0.100 (9)	57 (19)

[a] The form of the anisotropic thermal ellipsoids is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^* + \ldots)]$.

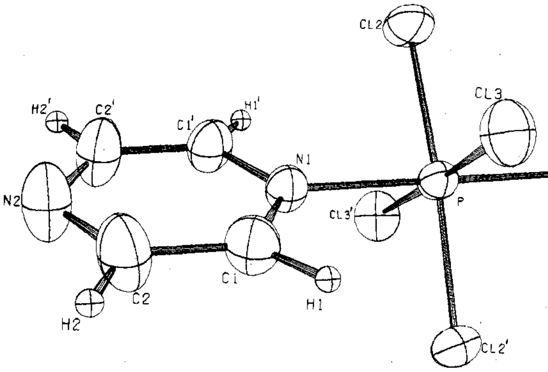

Figure 1. Molecular structure of pyz·PCl_5.

using the procedure of Levy, Busing and Wehe.[16] The transmission coefficients ranged from 0.67 to 0.94.

Phases were determined by using the symbolic addition procedure of Karle and Karle.[17] Least-squares refinement utilized anisotropic thermal parameters for the nonhydrogen atoms and isotropic thermal parameters for hydrogens. The final discrepancy index (R) based on the full data set is 0.097. The difference Fourier showed no peaks of chemical significance.

^1H NMR Spectra. Samples for NMR analysis were prepard by weighing the solutes in a drybox and vapor transferring dried solvents onto the solute on a vacuum line. The tubes were sealed under vacuum. All liquids were previously dried and distilled according to standard methods.[18] Solids were washed and freshly sublimed under vacuum. Spectra were recorded on either a Perkin-Elmer R24A or a Varian A60D nuclear magnetic resonance spectrometer.

Raman Spectra. Samples for solution Raman were prepared as described above for NMR. Flat bottom, 6-mm o.d. Pyrex sample tubes, which had been platinized around half of the circumference, were used. A Jarrell-Ash 25-300 spectrometer employing a Spectra-Physics He-Ne laser was used for the spectrum of solid py·PCl_5. Other spectra were recorded on a pulsed-laser Raman spectrometer with a gated detector, described elsewhere.[19]

Results and Discussion

Solid-State Structure. X-ray Data. The phosphorus atom of pyz·PCl_5 is octahedrally coordinated having one position occupied by a nitrogen atom of the pyrazine ring. See Figure 1. Atomic positions and thermal parameters are listed in Table I. Bond distances and angles are found in Table II.

The P–N bond length of 2.021 (5) Å is longer than similar P–N bonds found in the literature; Sheldrick has reported P–N bond lengths of 1.885 (4) and 1.911 (4) Å for py·PF_5 and 2-methyl-8-hydroxyquinoline–phosphorus(V) fluoride.[13] Our longer bond can be attributed in part to both the reduced acidity of PCl_5 compared to PF_5 and the decreased basicity of pyrazine compared to pyridine. Similar to the observation of Sheldrick on py·PF_5, the coplanar Cl atoms 2, 2′, 3, and 3′ lie closer to pyrazine than to Cl1. The equation of the least-squares plane is $16.20y = 5.447$ where x, y, and z are fractional coordinates in direct space. The phosphorus atom lies out of this plane by 0.08 Å. The average acute Cl–P–N angle, excluding Cl1, is 87.8° which is comparable to the corresponding angle in py·PF_5. The planar pyrazine ring ($4.775x + 5.424z = 1.356$) makes an angle of 46.0° with the Cl1, Cl2, Cl2′, P, N1 plane ($8.253x - 0.02879z = -0.00720$); in py·$PF_5$ this angle is 40.8°.[13] We find almost equal Cl···H intramolecular nonbonded contacts of 2.63 (6) and 2.53 (6) Å for Cl2···H1′ and Cl3···H1, respectively, which are 9% and 13% lower than the sum of the minimum van der Waals radii. Steric effects, therefore, do not lead to significant deviation in the orientation of the pyrazine ring from the expected value of 45°. Packing of the unit cell is shown in Figure 2. The shortest intermolecular Cl···H contact is 2.93 Å.

The P–Cl distances agree with those found in PCl_6^-,[20] with the exception of P–Cl1. Since chlorines 2, 2′, 3, and 3′ are

Table II. Bond Distances (Å) and Angles (Deg)

	Distances		
P–Cl1	2.088 (3)	N1–C1	1.353 (6)
P–Cl2	2.127 (2)	N2–C2	1.327 (8)
P–Cl3	2.126 (2)	C1–C2	1.390 (7)
P–N1	2.021 (5)	C1–H1	1.04 (7)
		C2–H2	0.89 (7)
	Angles		
Cl1–P–Cl2	92.4 (1)	C2–N2–C2′	116.3 (6)
Cl1–P–Cl3	91.9 (1)	N1–C1–C2	120.2 (5)
Cl2–P–Cl3	89.5 (1)	N2–C2–C1	123.0 (6)
Cl2–P–N1	87.6 (1)	N1–C1–H1	112.8 (35)
Cl3–P–N1	88.1 (1)	C2–C1–H1	126.8 (35)
P–N1–C1	121.4 (3)	C1–C2–H2	118.2 (45)
C1–N1–C1′	117.3 (5)	N2–C2–H2	118.7 (45)

Table III. Raman Frequencies of Solid py·PCl_5 and pyz·PCl_5

py·PCl_5[3]			this work	
calcd	found	tentative assignt	py·PCl_5	pyz·PCl_5
422	455 mw	a_1 $\nu(PCl_{ax})$	449 vw	455 w
	440 w, sh	ligand modes		
	360 ms			
358	351 vs	a_1 $\nu(PCl_{eq})$	350 vs	351 vs
276	287 mw, sh	a_1 $\delta(PCl)_{op}$	288 mw, sh	285 w, sh
275	276 ms	b_1 $\nu(PCl_{eq})$	276 ms	270 m
225	251 m	e $\delta(PCl_{ax})$	250 mw	244 mw, sh
			220 vw, sh	
242	210 vw	b_1 $\delta(PCl)_{ip}$	209 w	208 w
190	190 mw	a_1 $\nu(PN)$	189 mw	189 m
166	178 w	b_2 $\delta(PCl)_{op}$		
	109 ms		109 ms	
	100 m, sh		101 m, sh	
	80 w			

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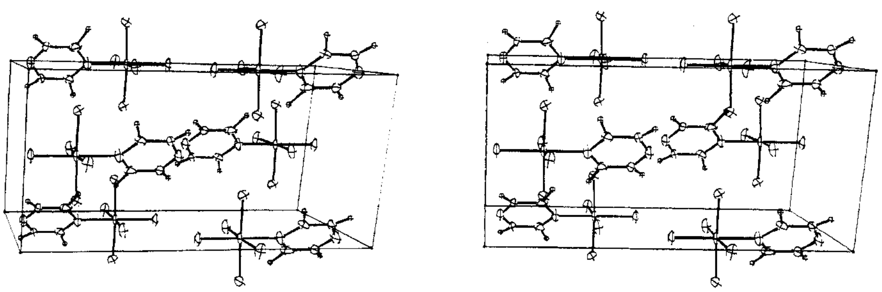

Figure 2. Stereoscopic view of the unit cell of pyz·PCl_5 looking down the *a* axis.

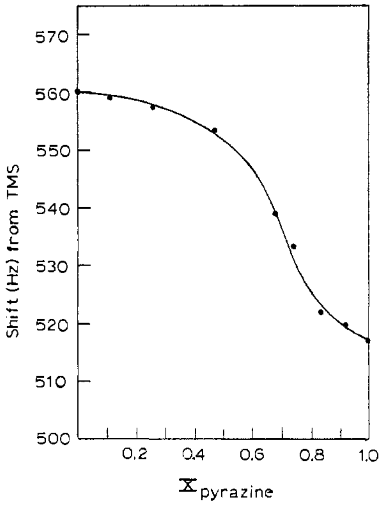

Figure 3. ^1H NMR shift from Me_4Si vs. mole fraction of pyrazine (X_{pyz}) for solutions of pyz·PCl_5 containing excess pyrazine.

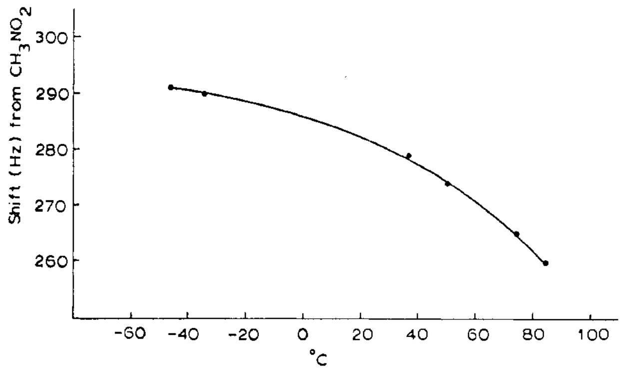

Figure 4. Temperature dependence of ^1H NMR shift expressed in Hz from CH_3NO_2 for pyz·PCl_5.

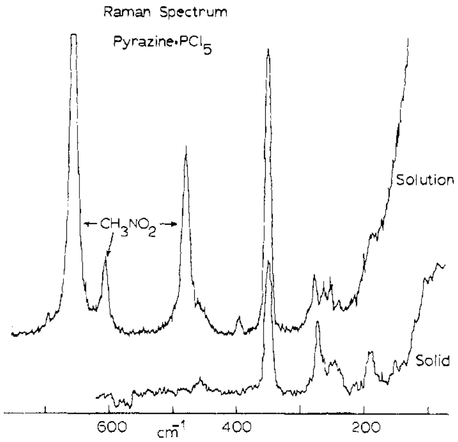

Figure 5. Raman spectrum of pyz·PCl_5 solid and CH_3NO_2 solution.

Table IV. Raman Frequencies below 700 cm^{-1} of 0.24 M pyz·PCl_5 in CH_3NO_2

695 w	pyrazine	348 s	pyz·PCl_5
655 vs	solvent	274 mw	pyz·PCl_5
604 m	solvent	262 mw	
478 s	solvent	250 mw	pyz·PCl_5
455 w, sh	pyz·PCl_5	238 w	
395 w	PCl_5	187 w, sh	pyz·PCl_5

shifted toward the pyrazine ring, Cl1 takes a position closer to P than it does in PCl_6^-.

Raman Spectra. Solid-state laser Raman spectra of pyz·PCl_5 and py·PCl_5 were obtained for comparison with the published[8] spectrum of py·PCl_5 and the solution spectrum of pyz·PCl_5 reported below. Three major differences are noted in the py·PCl_5 spectra shown in Table III. Beattie reports bands at 440 cm^{-1}, assigned to ligand modes, at 360 cm^{-1}, unassigned, and at 178 cm^{-1}, assigned to a P–Cl bending mode. We do not observe these bands in either py·PCl_5 or pyz·PCl_5. The 360- and the 178-cm^{-1} bands are probably due to ion impurities since the strongest band of solid phosphorus(V) chloride is at 359 cm^{-1}, assigned to PCl_6^-, and a strong PCl_4^+ band occurs at 177 cm^{-1}.[21] A very weak shoulder, which is absent from Beattie's spectrum, is seen at 220 cm^{-1} for py·PCl_5 and is unassigned. The remaining frequencies in Table III are in good agreement. The computed vibrational frequencies in Table III are based on the octahedral geometry about phosphorus.[8]

Solution Structure. Solution measurements in CH_3NO_2 indicate the presence of a variety of species, one of which is pyz·PCl_5. In an attempt to identify the species and further characterize a suggested exchange process,[14] we performed four experiments.

(1) Addition of Excess Pyrazine. Seven solutions containing variable quantities of pyz·PCl_5, pyz, and CH_3NO_2 were prepared for ^1H NMR analysis. The mole fraction of pyrazine (X_{pyz}) was computed on the basis of the assumption that the pyrazine in solution originated from the added excess and very little from the bound vs. free pyrazine exchange. A plot of X_{pyz} vs. NMR shift from Me_4Si is given in Figure 3. Solutions representing X_{pyz} = 0.0 and 1.0 are included in Figure 3. With increasing X_{pyz}, the single resonance shifts upfield toward that of free pyrazine in nitromethane. The resonance position approaches the limiting values of 560 and 517 Hz at X_{pyz} = 0.0 and 1.0 as expected for a system at equilibrium. Furthermore, this equilibrium is rapidly established relative to the NMR time scale, since an average resonance position is observed.

(2) Raman Spectrum of pyz·PCl_5 in Nitromethane. The Raman spectrum of a nitromethane solution 0.24 M in pyz·PCl_5 shows bands due to the adduct, pyrazine, and PCl_5. See Table IV and Figure 5. It will be noted in Table III and Figure 5 that the bands for the solid pyz·PCl_5 also appear in our solution spectrum. The 395-cm^{-1} band unobserved in the solid-state spectrum is assigned to molecular PCl_5, since the strongest Raman band of molecular PCl_5 appears at 395

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[21] Livingston, K.; Ozin, G. A. *J. Chem. Soc. A* **1969**, 2840.

cm^{-1}.[22] In addition, the most intense bands reported for pyrazine[23] are also observed in our solution spectrum at 695, 1009, 1220, and 3055 cm^{-1}.

In the region 200–300 cm^{-1}, four bands are observed for the solution spectrum, whereas for solid pyz·PCl_5 only two rather broad bands are seen. The additional solution bands may be assigned to ionization products of PCl_5 and pyz·PCl_5, but the species remain unidentified at this time. Since the equilibria $2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$ and $PCl_5 \rightleftharpoons PCl_4^+ + Cl^-$ have been shown to occur in CH_3NO_2,[22] the ionization of pyz·PCl_5 in CH_3NO_2 would not be surprising. In fact, ions of the type $(py)_2PCl_4^+$ have been stabilized in solutions of nitrobenzene by adding pyridine or substituted pyridines to $[PCl_4][SbCl_6]$.[10] The ionicity is further substantiated by the fact that 0.7 M solutions of the adduct in CH_3NO_2 exhibit conductivity of 14.5 Ω^{-1} cm^2 mol^{-1} at 25 °C.[14]

(3) Variable-Temperature ^{1}H NMR Spectrum. If equilibria involving pyz·PCl_5, pyz, PCl_5, and ions are operative, a change in temperature might result in a change in the relative amounts of complexed and free pyrazine. A solution containing 0.03 M pyz·PCl_5 in a mixed solvent, nitromethane and 1-nitropropane (used in order to access lower temperatures), was prepared and the ^{1}H NMR spectrum recorded in the range −46 to +85 °C. Figure 4 illustrates the shift observed for the single pyrazine resonance relative to CH_3NO_2. Below room temperature the resonance shifts downfield, away from that of free pyrazine; above room temperature, the resonance shifts upfield toward that of free pyrazine. This reversible-temperature dependence of the pyrazine NMR shift indicates that the equilibrium or equilibria are exothermic in the direction of the bound pyrazine. The same observations are made by using nitromethane as solvent, although the lowest temperature accessible is only −28 °C.

Because our freezing-point measurements show a twofold increase in the number of solute particles, the bound pyrazine observed in the low-temperature ^{1}H NMR experiment cannot simply be pyz·PCl_5. The species responsible for this increase of solute particles could include the ionization products of PCl_5 and/or pyz·PCl_5. The ^{1}H NMR experiment would not distinguish between the resonance of pyz·PCl_5 and its ionization product because pyrazine is coordinated to phosphorus in both cases and an average proton environment is observed due to exchange.

(4) Addition of Dimethylammonium Chloride. In our earlier report[14] we have suggested the involvement of Cl^- in a solution equilibrium. If so, addition of Cl^- should perturb the equilibrium, thereby affecting the relative amounts of complexed and uncomplexed pyrazine. To examine this possibility, we prepared a solution containing 0.15 M pyz·PCl_5 and 0.30 M dimethylammonium chloride in nitromethane. The single pyrazine ^{1}H NMR resonance shifted 22 Hz upfield away from the resonance position of the complex, while the spectrum of dimethylammonium ion remained unchanged. This observation can be accounted for by considering an equilibrium (eq 1) similar to that suggested by Waddington et al.[9] for py·PCl_5

$$\text{py}\cdot PCl_5 + Cl^- \rightleftharpoons \text{py} + PCl_6^- \qquad (1)$$

in the presence of tetra-*n*-pentylammonium chloride in nitrobenzene. They observed two ^{31}P NMR resonances, one for py·PCl_5 and one for PCl_6^-. Our observation for the pyrazine system is indicative of a more rapidly established equilibrium relative to the NMR time scale, since only a single ^{1}H NMR resonance is observed.

It has also been suggested that pyz·PCl_5 is essentially completely associated at ambient temperatures in nitrobenzene on the basis of ^{31}P NMR data.[9] A 1:1 solution of pyrazine and PCl_5 in nitrobenzene exhibits a lower chemical shift, 219.1 ppm, than a solution saturated in excess pyrazine, 224.9 ppm. We suggest that this lower chemical shift is the result of a rapidly established solution equilibrium which may involve the species PCl_5, pyz·PCl_5, and ionization products. The average environment for phosphorus observed by the ^{31}P NMR experiment would yield a resonance position of lower chemical shift than that of a solution containing only 6-coordinate phosphorus.

Summary

The solid-state structure of pyz·PCl_5 is octahedral with a long P–N bond, 2.021 Å. This species is in equilibrium in CH_3NO_2 solution with PCl_5 and pyrazine. An equilibrium scheme in nitromethane must account for the apparent doubling of solute particles at the freezing point, the existence of ions at 25 °C, the ^{1}H NMR shifts discussed above, and the Raman spectrum. It appears that three chemical processes may be occurring in solutions of pyz·PCl_5 in CH_3NO_2: substitution, dissociation, and ionization. Substitution involves eq 1 which is supported by our ^{1}H NMR data. Dissociation requires an equilibrium between complexed and uncomplexed pyrazine represented by eq 2. Our Raman spectrum identifies

$$PCl_5 + \text{pyz} \rightleftharpoons \text{pyz}\cdot PCl_5 + \text{heat} \qquad (2)$$

these species, and ^{1}H NMR experiments on solutions containing excess pyrazine support the proposal of an equilibrium. Ionization of PCl_5 and/or pyz·PCl_5 account for the conductivity, cryoscopic molecular weight, and low-temperature ^{1}H NMR measurements, although the specific ions present in solution are not proven.

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Registry No. pyz·PCl_5, 64537-03-7; py·PCl_5, 18534-27-5.

Supplementary Material Available: A listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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