is surrounded by ten hydrogen atoms at distances from 3.00 to 3.34 A; the next nearest neighbors to the cesium atom are two boron atoms, B(10), at 3.67 A.

The framework of the $(B_9C_2H_{11})_2Co^-$ group is shown in Figure 1. The structure consists of two icosahedra in a staggered configuration joined at a common apex, which is the cobalt atom. The two carbon atoms are shown in disordered positions in the pentagon of atoms adjacent to the cobalt, occupying mainly positions 2, 3, 5, and 6. The interatomic distances in the framework are shown in Figure 2.

Each atom with the exception of cobalt in the framework shown in Figure 1 has bonded to it a hydrogen atom. The hydrogen bond lengths are shown in Table III; the differences among them are not experimentally significant.

The above icosahedral structure is very similar to that found in $(B_9C_2H_{11})Fe(C_5H_5)$[7] and in $(B_9C_2H_{11})Re(CO)_3$,[6] where there is no disorder of the carbon atoms. Because of the disorder in $(B_9C_2H_{11})_2CoCs$, we cannot say if the carbon atoms are adjacent or not in each molecule, nor indeed if the crystal contains a single isomer or more than one isomer.

Table IV shows a list of angles in the $(B_9C_2H_{11})_2Co^-$ group.

Acknowledgment.—We wish to thank Professor M. F. Hawthorne and Dr. T. D. Andrews for providing us with the interest and the crystals that made this work possible.

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Notes

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The Preparation and Some Reactions of Phosphoramidic Difluoride[1]

BY SANTAD KONGPRICHA AND WILLIAM C. PREUSSE

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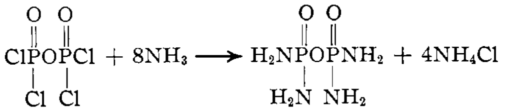
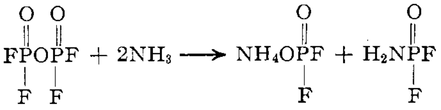
The reaction of ammonia with pyrophosphoryl tetrachloride[2] was previously reported to give pyrophosphoryl tetramide, $P_2O_3(NH_2)_4$. In this reaction the preferential attack by ammonia on the P–Cl bond rather than the P–O–P bond was noted



$$\mathrm{Cl}\overset{\mathrm{O}}{\underset{\mathrm{Cl}}{\mathrm{P}}}\mathrm{O}\overset{\mathrm{O}}{\underset{\mathrm{Cl}}{\mathrm{P}}}\mathrm{Cl} + 8\mathrm{NH_3} \longrightarrow \mathrm{H_2N}\overset{\mathrm{O}}{\underset{\mathrm{H_2N}}{\mathrm{P}}}\mathrm{O}\overset{\mathrm{O}}{\underset{\mathrm{NH_2}}{\mathrm{P}}}\mathrm{NH_2} + 4\mathrm{NH_4Cl}$$

The recently published facile preparation of pyrophosphoryl tetrafluoride[3] prompted us to investigate its reaction with ammonia to determine whether the substitution of the phosphorus-bonded fluorine atoms by amido groups or the heterolytic cleavage of the P–O–P bond by ammonia occurred predominantly.

When pyrophosphoryl tetrafluoride was treated with ammonia, ammonium difluorophosphate[4,5] and phosphoramidic difluoride were obtained

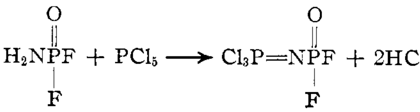


$$\mathrm{F}\overset{\mathrm{O}}{\underset{\mathrm{F}}{\mathrm{P}}}\mathrm{O}\overset{\mathrm{O}}{\underset{\mathrm{F}}{\mathrm{P}}}\mathrm{F} + 2\mathrm{NH_3} \longrightarrow \mathrm{NH_4O}\overset{\mathrm{O}}{\underset{\mathrm{F}}{\mathrm{P}}}\mathrm{F} + \mathrm{H_2N}\overset{\mathrm{O}}{\underset{\mathrm{F}}{\mathrm{P}}}\mathrm{F}$$

The novel phosphoramidic difluoride was characterized by infrared and ^{31}P and ^{19}F nuclear magnetic resonance spectrometry. The reaction of ammonia with pyrophosphoryl tetrafluoride is indeed different from that with pyrophosphoryl tetrachloride. The highly electronegative fluorine atoms in $P_2O_3F_4$ probably withdraw electrons toward themselves, thus weakening the POP bond. Since phosphoryl trifluoride[6] in ethyl ether reacted rapidly with ammonia, even at −110°, to form phosphoryl triamide, phosphoramidic difluoride would, thus, be expected to react further with excess of ammonia.

The reactions of phosphoramidic difluoride with phosphorus pentachloride and with triphenylphosphorus dichloride were investigated.

Phosphoramidic difluoride reacted with an equivalent amount of phosphorus pentachloride to yield trichlorophosphazophosphoryl difluoride



$$\mathrm{H_2N}\overset{\mathrm{O}}{\underset{\mathrm{F}}{\mathrm{P}}}\mathrm{F} + \mathrm{PCl_5} \longrightarrow \mathrm{Cl_3P{=}N}\overset{\mathrm{O}}{\underset{\mathrm{F}}{\mathrm{P}}}\mathrm{F} + 2\mathrm{HCl}$$

Its infrared spectrum is quite similar to that of $Cl_3P{=}NPOCl_2$[7] (mp 35.5°; bp 102° (1 mm)), except for the additional P—F stretching frequency in $Cl_3P{=}NPOF_2$.

Trichlorophosphazophosphoryl difluoride decomposed in an atmosphere of nitrogen at 200° to liberate gaseous products which were mainly OPF_2Cl and $OPCl_3$. The residue was an opaque elastomeric material with an empirical formula of $(NPFCl)_n$. It was not determined if the elastomer was a mixture of

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(1) Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964; Abstracts, p 3K.

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$(\mathrm{NPCl_2})_n$ and $(\mathrm{NPF_2})_n$ or actually $(\mathrm{NPClF})_n$. The decomposition reactions were probably

$$n\mathrm{Cl_3P{=}NPOF_2} \longrightarrow (\mathrm{Cl_2PN})_n + n\mathrm{OPF_2Cl}$$

and

$$n\mathrm{Cl_3P{=}NPOF_2} \longrightarrow n\mathrm{Cl_3PO} + (\mathrm{NPF_2})_n$$

The halogen exchange between the products also could not be ruled out. The nature of the decomposition of $\mathrm{Cl_3P{=}NPOF_2}$ certainly requires further elucidation.

Triphenylphosphazophosphoryl difluoride was obtained when phosphoramidic difluoride and triphenylphosphorus dichloride were heated in carbon tetrachloride

$$\mathrm{H_2NPOF_2} + (\mathrm{C_6H_5})_3\mathrm{PCl_2} \longrightarrow (\mathrm{C_6H_5})_3\mathrm{P{=}NPOF_2} + 2\mathrm{HCl}$$

No attempts were made to polymerize the $(\mathrm{C_6H_5})_3\mathrm{P{=}NPOF_2}$, although $(\mathrm{C_6H_5})_2\mathrm{ClP{=}NPOCl_2}$[8] was reported to form no polymer when heated to 220° either *in vacuo* or at atmospheric pressure.

Experimental Section

Nuclear Magnetic Resonance Spectra.—The ^{1}H nmr spectrum was obtained with a Varian A-60 spectrometer operating at 60 Mcps. The value for the chemical shift is given in ppm (parts per million) relative to tetramethylsilane.

The ^{31}P and ^{19}F nmr spectra were recorded on a Varian HR-60 spectrometer, ^{31}P at 19.3 Mcps and ^{19}F at 56.4 Mcps. The values for the chemical shift in ppm are in reference to external 85% $\mathrm{H_3PO_4}$ for ^{31}P and to internal $\mathrm{CCl_3F}$ for ^{19}F. The double irradiation to decouple ^{1}H from ^{31}P and ^{31}F was performed with an NMR Specialties SD-60 heteronuclear decoupler operating at 60 Mcps.

Phosphoramidic Difluoride.—Ammonia (19 g, 1.12 moles), dried with sodium, was slowly bubbled, with constant stirring, through a solution of pyrophosphoryl tetrafluoride[3] (107 g, 0.575 mole) in 400 ml of anhydrous ethyl ether at −78°. When all of the ammonia was used, the reaction mixture was filtered. The precipitate was washed twice with anhydrous ethyl ether. Then it was extracted with absolute ethyl alcohol. The alcohol solution was evaporated to dryness *in vacuo* to yield ammonium difluorophosphate (60 g, 87.8%); mp 190–192° (lit.[4] 213°).

Anal. Calcd for $\mathrm{H_4NPO_2F_2}$: F, 31.92; N, 11.77; P, 26.02. Found: F, 31.9; N, 11.8; P, 25.5.

The infrared spectrum of the compound was in accordance with that reported by Corbridge and Lowe.[5]

The crude liquid product obtained from evaporation of the ether filtrates was purified by fractional distillation under vacuum to give moisture-sensitive phosphoramidic difluoride (30 g, 53.2%); mp 27–28°; bp 69° (0.18 mm).

Anal. Calcd for $\mathrm{H_2NPOF_2}$: F, 37.6; N, 13.9; P, 30.7. Found: F, 37.8; N, 14.2; P, 30.1.

$\mathrm{H_2NPOF_2}$ dissolved in water with vigorous reaction. When heated to 140–160°, it started to decompose with liberation of HF.

The infrared spectrum of $\mathrm{H_2NPOF_2}$ showed the expected $\mathrm{NH_2}$ absorptions[9] ($\mathrm{cm^{-1}}$) at 3300 (s, stretching) and 1560 (m, deformation), as well as the P=O absorptions[9] at 1310 (s, stretching) and 1075 (m, stretching), and P—F absorptions[9] at 915 (s, stretching) and 848 (m, stretching).

The ^{1}H nmr of $\mathrm{H_2NPOF_2}$ in ethyl ether solution appeared as a broad band centered at −5.5 ppm. The ^{1}H nmr spectrum[10] of the $\mathrm{NH_2}$ group in $\mathrm{H_2NPS(CH_3)_2}$ was reported to be at −3.47 (broad) ppm. Broadening of the spectrum is probably due to quadrupole coupling[11] of ^{14}N with ^{1}H and spin coupling of ^{31}P and ^{19}F with ^{1}H.

The ^{31}P nmr spectrum consisted of a triplet, due to spin coupling with ^{19}F, having a coupling constant, J_{PF}, of 983 cps and being situated at +1.2 ppm. The J_{PF} in $\mathrm{(HO)POF_2}$ was reported as 984 cps.[12] Each band in the triplet was further split into triplets because of spin coupling with ^{1}H, having a J_{PH} of 5 cps. Irradiation of the ^{1}H at 60 Mcps while measuring the ^{31}P nmr spectrum resulted in a collapse of the 5-cps splitting.

The ^{19}F nmr spectrum of $\mathrm{H_2NPOF_2}$, taken while the ^{1}H was being decoupled by irradiation at 60 Mcps, showed two bands which were separated by 981 cps. This is in accordance with J_{FP} of 978 cps in $\mathrm{(HO)POF_2}$.[12] When the irradiation was removed, the spectrum consisted of two triplets with J_{FH} of 2 cps and J_{FP} of 981 cps. The ^{19}F chemical shift was +73.43 ppm.

Trichlorophosphazophosphoryl Difluoride.—Phosphoramidic difluoride (16.8 g, 0.1665 mole) and phosphorus pentachloride (34.7 g, 0.166 mole) in 150 ml of 1,1,2,2-tetrachloroethane were heated with constant stirring to about 120–125° for 5 hr. The reaction solvent was then removed *in vacuo* and the resulting crude liquid product was purified by vacuum fractional distillation to give $\mathrm{Cl_3P{=}NPOF_2}$ (38.8 g, 50.2% yield); mp 12–14°; bp 44° (1.2 mm).

Anal. Calcd for $\mathrm{Cl_3PNPOF_2}$: Cl, 45.01; F, 16.08; N, 5.93; P, 26.21. Found: Cl, 44.8; F, 16.0; N, 5.78; P, 25.52.

The infrared spectrum of $\mathrm{Cl_3P{=}NPOF_2}$ showed one of the strong absorption bands at 1350 $\mathrm{cm^{-1}}$ which is attributable to the P=N group.[13] Other characteristic absorption bands ($\mathrm{cm^{-1}}$) were at 1300 (s, P=O stretching),[9] 910 (s, P—F stretching),[9] and 765 (m).

$\mathrm{Cl_3P{=}NPOF_2}$ dissolved in water with exothermic reaction. It had a density of 1.7873 g/ml at 27°. Its vapor pressure data (43°, 1.1 mm; 80°, 9.0 mm; 116°, 50 mm; 134°, 100 mm; 143°, 140 mm) are summarized by the equation $\log p(\mathrm{mm}) = 8.8106 - (2769/T)$. When heated in an atmosphere of nitrogen, it decomposed slowly at 160° and rapidly at 200° with liberation of gases, leaving an elastomeric residue. Mass spectral analysis of the gaseous products showed them to be mainly $\mathrm{OPF_2Cl}$ and $\mathrm{OPCl_3}$, as well as small amounts of $\mathrm{OPFCl_2}$ and $\mathrm{OPF_3}$. The elastomer was insoluble in organic solvents such as ether and carbon tetrachloride and was thermally stable up to 350°. It was, however, unstable with respect to hydrolysis.

Anal. Calcd for $(\mathrm{NPClF})_n$: Cl, 35.66; F, 19.10; N, 14.09; P, 31.15. Found: Cl, 28.9; F, 13.0; N, 12.65; P, 30.4.

Triphenylphosphazophosphoryl Difluoride.—Triphenylphosphorus dichloride (14 g, 0.042 mole) and phosphoramidic difluoride (10 g, 0.099 mole) in 50 ml of carbon tetrachloride were heated, with constant stirring, to boiling under total reflux for 4 hr. When the liberation of hydrogen chloride ceased, the reaction mixture was filtered and the white precipitate washed with ether. The solid product was further purified by extraction with benzene and recrystallization of the benzene-soluble product from benzene to yield triphenylphosphazophosphoryl difluoride (6.53 g, 43%); mp 191–193°.

Anal. Calcd for $(\mathrm{C_6H_5})_3\mathrm{PNPOF_2}$: C, 59.8; H, 4.16; F, 10.5; N, 3.88; P, 17.2. Found: C, 59.6; H, 4.28; F, 10.9; N, 3.93; P, 17.2.

The characteristic infrared absorptions ($\mathrm{cm^{-1}}$) of $(\mathrm{C_6H_5})_3\mathrm{P{=}NPOF_2}$ are: P=N at 1340 (s); P=O at 1260 (s); P—F at 885 (s); $\mathrm{P{-}C_6H_5}$ at 1380 (m, sharp) and 1000 (m, sharp); and C—H in $\mathrm{C_6H_5}$ at 3100 (w).

Acknowledgment.—We wish to thank Mr. G. D. Vickers and Dr. H. Agahigian for their assistance in

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obtaining and interpreting the nuclear magnetic resonance spectra, Dr. H. D. Hoberecht for mass spectral analyses, and Dr. R. C. Rittner for elemental analyses.

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A Study of the Temperature Dependence of the Dipole Moment of Dichlorobis(acetylacetonato)tin(IV)

BY VERA DORON[1] AND CHAVA FISCHER

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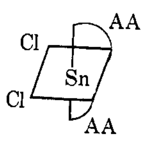
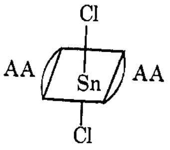
The stereochemistry of bis(acetylacetonato)tin(IV) complexes has been the subject of a number of recent publications.[2-6]

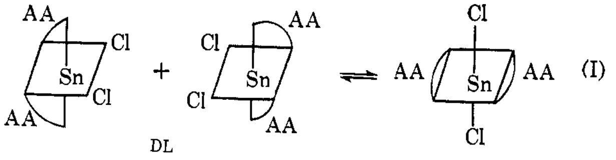
The *cis* structure (Ia) for dichlorobis(acetylacetonato)tin(IV) has been proposed on the basis of nmr evidence[3] alone. Dipole moment measurements carried out by the present authors and others[7] seem to be in agreement with the earlier proposed structure. It should be pointed out at this time that related compounds of tin such as $(C_6H_5)_2Sn(AA)_2$ (AA = acetylacetonate) have been assigned[6] the *trans* configuration in solution though a dipole moment of approximately 4 D. was reported. Whether this moment is due to a high induced polarization as suggested[6] or whether there is a permanent moment present can only be decided by a study of the temperature dependence of the dipole moment.



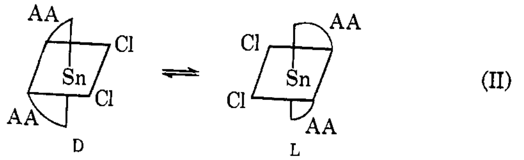
Ia



Ib



(I)



(II)

The present study was initially undertaken in an effort to shift a possible *cis–trans* (I) equilibrium which may occur in solution. The data indicate that within the temperature range (30–79°) no shift occurs as evidenced by the constant value of the dipole moment (Table I).

TABLE I

THE DIPOLE MOMENTS OBTAINED FOR $Sn(AA)_2Cl_2$ AT VARIOUS TEMPERATURES

Temp, °C	$(\Delta/C)_0$	C_2	$\epsilon_{12} - n_{12}^2$	μ, D.[d,e]
30[a]	5.789×10^3	1.90×10^{-5}	1.10×10^{-1}	6.90
34[b]	5.148×10^3	2.35×10^{-6}	1.21×10^{-2}	6.57
77.5[a]	4.048×10^3	2.10×10^{-6}	8.5×10^{-3}	6.35
79[c]	4.413×10^3	2.90×10^{-6}	1.28×10^{-2}	6.65

[a] Measurements were carried out on freshly prepared solutions at the given temperatures. [b] The solution was equilibrated at 79° for 3 days and rapidly cooled to the given temperature. [c] The solution was equilibrated at 79° for 3 days; then measurements were carried out at the given temperature. [d] The dipole moments were calculated using the equation

$$\mu^2 = \text{constant}\left(\frac{T}{(\epsilon_1 + 2)(n_1^2 + 2)}\right)\left(\frac{\Delta}{C_2}\right)_0$$

where constant $= 27k/4\pi N$ and $k = 1.38 \times 10^{-16}$, $N = 6.02 \times 10^{23}$, and T varies as indicated in the table. $(\Delta/C_2)_0$ is the value of the slope obtained by plotting C_2, the concentration of solute in moles/ml of solution, against Δ, where $\Delta = \epsilon_{12} - n_{12}^2$ and ϵ_{12} and n_{12} are the dielectric constant and refractive index of the measured solution, respectively. ϵ_1 and n_1 are the dielectric constant and refractive index, respectively, of the solvent. The slope is obtained by extrapolation of the straight line to concentration $C_2 = 0$. [e] All measurements were obtained on sublimed material. The sublimation was carried out either around 170° at 1–2 mm or around 185° at atmospheric pressure. Nelson[7b] obtained the same value for the moment (6.77 D.) on nonsublimed material at room temperature.

Dipole moments were measured in benzene solutions by following the concentration dependence of the dielectric constant[8] and refractive indices.[9] Calculations were based on the methods of Guggenheim[10] and Smith.[11] The contribution of induced and orientation polarization to the total polarization of dichlorobis(acetylacetonato)tin(IV) at 30° is approximately 14 and 86%, respectively, as calculated by using the Debye equation.

The constant value of the dipole moments obtained, with strong evidence for the *cis* (Ia) structure in solution, then suggests that a *cis–cis* (II) equilibrium is most probably the prevailing one in solution. The dipole moment data are in good agreement with the data of Faller and Davison,[4] who have shown by means of temperature-dependent nmr studies that a rapid equilibrium is involved at approximately 90° and that this is most likely the *cis–cis* (II) interconversion of the two enantiomeric forms.

The mean deviation among the obtained moments is ±0.28 D. (Table I). The deviations between

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