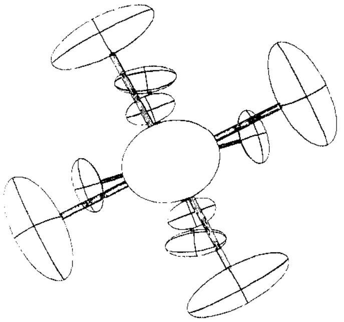

Figure 3.—A perspective drawing of $S_2N_2(SbCl_5)_2$ which shows the relative orientations of the $S_2N_2$ ring and the $SbCl_5$ groups. The view is down the *a* axis, from $Sb_2$ to $Sb_1$. The horizontal axis is $-c$; the vertical axis is $+b$.

thermal ellipsoids for the equatorial chlorine atoms, shown in Figures 1 and 3.

The octahedral geometry of the N–$SbCl_5$ groups is distorted by a shift of the equatorial chlorines toward the nitrogen donor atom such that the $Cl_{eq}$–Sb–N angles are all less than 90° whereas the $Cl_{eq}$–Sb–$Cl_{ax}$ angles are correspondingly larger than 90°. This tendency of the equatorial chlorines to move in toward the donor atom is characteristic of $SbCl_5$ adducts. For example, $SbCl_5 \cdot SeOCl_2$,[10] $SbCl_5 \cdot S_4N_4$,[13] and $SbCl_5 \cdot CH_3CN$[22] exhibit average $Cl_{eq}$–Sb–donor atom angles of 86.2, 89.0, and 84.9°, respectively. The average Sb–Cl bond length in $S_2N_2(SbCl_5)_2$, 2.305 (3) Å, falls at the short end of the range of distances previously reported for similar adducts. Some of these are: $SbCl_5 \cdot SO_2(CH_3)_2$, 2.32 Å;[10] $SbCl_5 \cdot POCl_3$, 2.33 Å;[11] $SbCl_5 \cdot SeOCl_2$, 2.34 Å;[10] $SbCl_5 \cdot PO(CH_3)_3$, 2.34 Å;[11] $SbCl_5 \cdot SO(C_6H_5)_2$, 2.35 Å;[10] $SbCl_5 \cdot CH_3CN$, 2.36 Å;[22] $SbCl_5 \cdot S_4N_4$, 2.39 Å.[13] The $SbCl_5$ bond lengths reported for solid antimony pentachloride at −30° are 2.29 Å for the three basal chlorines and 2.34 Å for the two apical chlorines (average 2.31 Å).[9]

Table VII

| | $S_4N_4 \cdot SbCl_5$[a] | $CH_3CN \cdot SbCl_5$[b] | $S_2N_2$-$(SbCl_5)_2$[c] | $SbCl_5$[d] |
|---|---|---|---|---|
| N–Sb, dist, Å | 2.17 | 2.23 | 2.283 | |
| Sb–Cl dist, Å | 2.39 | 2.36 | 2.305 | 2.31 |
| $Cl_{eq}$–Sb–N, deg | 89.0 | 84.9 | 83.04 | |

[a] Reference 13. [b] Reference 22. [c] This work. [d] Reference 9.

We find, then, that in comparison with known structures of similar adducts of $SbCl_5$ with Lewis bases, $S_2N_2(SbCl_5)_2$ contains the longest Sb–N bond, the shortest Sb–Cl bonds, and the greatest displacement of the equatorial chlorines toward the donor atom (smallest average $Cl_{eq}$–Sb–donor atom angle). It appears that all three properties are functions of the strength of the adduct, and the data summarized in Table VII show that $S_2N_2(SbCl_5)_2$ is then the weakest such adduct reported to date. This correlation is apparently a general property of electron donor–acceptor complexes. In a recent review of this type of complex, Prout and Wright[21] presented an analogous table of these properties for a series of N–$BF_3$ adducts which showed the same trends with increasing donor strength that we describe here for N–$SbCl_5$ adducts.

**Acknowledgment.**—We thank Professor William L. Jolly for his interest in this work and Professor David Templeton and Dr. Allen Zalkin for the use of their laboratory facilities. R. L. P. expresses his thanks to the United States Atomic Energy Commission for support through the Lawrence Radiation Laboratory Inorganic Materials Research Division.

(22) H. Binas, *Z. Anorg. Allgem. Chem.*, **352**, 271 (1967).

---

Contribution from the Department of Chemistry,
McGill University, Montreal 110, Quebec, Canada

# Preparation and Nuclear Quadrupole Resonance Interpretation of the Structure of *cyclo*-Tri-μ-nitrido-dichlorophosphorusbis(oxochlorosulfur)

By RUTH CLIPSHAM, R. M. HART, and M. A. WHITEHEAD

*Received March 4, 1969*

A new preparation of *cyclo*-tri-μ-nitrido-dichlorophosphorusbis(oxochlorosulfur), $NPCl_2(NSOCl)_2$, based on a pyrolytic decomposition of the product of a Kirsanov reaction between a linear phosphonitrilic chloride and sulfamic acid is presented. The infrared spectrum of $NPCl_2(NSOCl)_2$ in polar solution is similar to that of the solid state but relative intensities and positions of some of the bands in the solution spectra are solvent polarity dependent. The $^{35}Cl$ nuclear quadrupole resonance spectrum complements the known crystal structure and its temperature dependence provides additional evidence of the departure of molecular symmetry from $C_s$ in the solid state. The interactions are assigned and interpreted by comparison with those of other cyclic inorganic systems.

## Introduction

There has been considerable interest in the structure and properties of cyclic phosphonitrilic halides, though no consensus has been reached concerning the bonding involved in such compounds. Cyclic trimeric sulfanuric halides have also been reported and characterized. A preparation of the title compound, $NPCl_2(NSOCl)_2$, was reported by van de Grampel and Vos in 1963.[1] It can be thought of as a ring composed of

(1) J. C. van de Grampel and A. Vos, *Rec. Trav. Chim.*, **82**, 246 (1963).

units of both types and this has been confirmed in the X-ray study.[2] The work discussed in this article was performed during the course of an investigation into the preparation and characterization of such mixed rings in an attempt to gain further insight into the bonding involved in inorganic compounds containing phosphorus and/or sulfur atoms.

The preparation reported by van de Grampel and Vos is based on a pyrolytic decomposition of trichlorophosphazosulfonyl chloride ($\mathrm{Cl_3PNSO_2Cl}$, mp 32–36°, purified). This decomposition has been reported originally to yield a mixture of cyclic trimeric sulfanuric chlorides[3] and a subsequent report has confirmed this.[4] All of our attempts to prepare the mixed ring, as reported by van de Grampel and Vos, were unsuccessful. However, pyrolytic decomposition of unpurified trichlorophosphazosulfonyl chloride (slush at room temperature) produced a mixture of $\alpha$-sulfanuric chloride, $\alpha$-$\mathrm{(NSOCl)_3}$ (crude yield, 25%), and the mixed ring $\mathrm{NPCl_2(NSOCl)_2}$ (crude yield, 10%). Separation of the mixed ring could be achieved only after a long process of fractional crystallization with considerable loss.

An alternative method of preparation was discovered which yields the mixed ring without the concurrent production of cyclic trimeric sulfanuric chlorides. The product of a Kirsanov reaction between trichloro[(trichlorophosphoranylidene)amino]phosphorus(V) hexachlorophosphate, $[\mathrm{Cl_3PNPCl_3^+}][\mathrm{PCl_6^-}]$, and sulfamic acid, $\mathrm{NH_2SO_2OH}$, is a liquid consisting of phosphorus oxytrichloride, an impure substance which may be a linear compound, $\mathrm{Cl_3PNPCl_2NSO_2Cl}$, by analogy with the preparation of trichlorophosphazosulfonyl chloride.[5] The reaction proceeds in a manner similar to that preparation. Attempts to purify this product failed as it decomposes with further polymerization on distillation. However, if the decomposition is carried out at low pressures (1 mm) and temperatures of about 150°, $\mathrm{POCl_3}$ is liberated and $\mathrm{NPCl_2(NSOCl)_2}$ can be isolated from the polymeric residue remaining. Similarly, it is possible to obtain the mixed ring by starting with[6] $[\mathrm{Cl_3PNPCl_2NPCl_3^+}][\mathrm{PCl_6^-}]$. $\mathrm{NPCl_2(NSOCl)_2}$ can be obtained in crude form by extraction from the residue with carbon tetrachloride and purified by recrystallization of the crude material from nonpolar solvents or by vacuum sublimation (50–60°, 1 mm). It is stable to hydrolysis by atmospheric moisture in the solid state. In solution, however, particularly in polar solvents, it is susceptible to hydrolysis.

## Experimental Section

**Materials.**—All chemicals used were reagent grade. Carbon tetrachloride used for extraction was dried over calcium hydride at room temperature. Spectrograde solvents were used for recrystallizations and solution infrared measurements. Sulfamic acid was dried over phosphorus pentoxide prior to use. Ammonium chloride was dried at 120° and then stored over silica gel. Phosphorus pentachloride and ammonium chloride used in the initial reaction step were pulverized and weighed in a glove bag under dry $\mathrm{N_2}$ atmosphere. Sulfamic acid when required was weighed in the glove bag and then transferred to a drybox for pulverization and addition to the linear phosphonitrilic chloride product. All reactions and manipulations of products were carried out under moisture-free conditions until the crude mixed-ring product was obtained.

**$[\mathrm{Cl_3PNPCl_3^+}][\mathrm{PCl_6^-}]$ and $[\mathrm{Cl_3PNPCl_2NPCl_3^+}][\mathrm{PCl_6^-}]$.**—These linear phosphonitrilic chlorides were prepared from the controlled reaction of $\mathrm{PCl_5}$ with $\mathrm{NH_4Cl}$ according to the methods outlined by Becke-Goehring and Lehr.[6,7] Without further purification of reagent grade solvents, *sym*-tetrachloroethane and nitrobenzene, yields of 85% $[\mathrm{Cl_3PNPCl_3^+}][\mathrm{PCl_6^-}]$ and 25% $[\mathrm{Cl_3PNPCl_2NPCl_3^+}][\mathrm{PCl_6^-}]$ were obtained from the appropriate preparations.

**$\mathrm{NPCl_2(NSOCl)_2}$.**—The mixed ring was prepared by a series of reactions starting with $[\mathrm{Cl_3PNPCl_3^+}][\mathrm{PCl_6^-}]$ or $[\mathrm{Cl_3PNPCl_2NPCl_3^+}][\mathrm{PCl_6^-}]$. The linear phosphonitrilic chloride was subjected to a Kirsanov reaction in a 1:1 molar ratio with sulfamic acid. The resulting product was pyrolyzed for many hours, after which $\mathrm{NPCl_2(NSOCl)_2}$ was isolated from the polymeric reaction product. For example, 120 g of $[\mathrm{Cl_3PNPCl_3^+}][\mathrm{PCl_6^-}]$ and 21.8 g of $\mathrm{NH_2SO_2OH}$ were heated at 100° in a 500-ml round-bottomed flask fitted with a condenser until the reaction mixture had liquefied and most bubbling from the production of HCl had ceased. Total reaction time was approximately 6 hr. The product, a pale yellow viscous liquid containing granules of unreacted $\mathrm{NH_2SO_2OH}$, was filtered under dry $\mathrm{N_2}$. Using dried carbon tetrachloride for washing, the filtrate was transferred to a single-necked, round-bottomed 500-ml flask fitted with a Vigreux column, distillation head, and condenser. This was connected to a Dry Ice–ethanol slush trap leading to a vacuum pump. The contents of the flask were heated slowly at approximately 1 mm pressure until all the carbon tetrachloride and most of the $\mathrm{POCl_3}$ from the Kirsanov reaction had been collected in the slush trap. Then the temperature was raised to about 155° (oil bath temperature) and pyrolysis begun. The liquid gradually became more brown and viscous as decomposition proceeded until, after a total heating time of approximately 32 hr, the polymeric residue began to foam. When the flask was cooled and brought to atmospheric pressure with dry $\mathrm{N_2}$, treelike crystal formations appeared on the upper portions of the flask. During the pyrolysis, the liquid which refluxed in the column was first colorless and then gradually became bright yellow. $\mathrm{POCl_3}$ from the decomposition was collected in the slush trap with a small amount of yellow-orange material which was not characterized.

The crystalline material was scraped from the column or extracted with the flask contents in warm carbon tetrachloride. After evaporation of the solvent in the atmosphere, needlelike crystals of $\mathrm{NPCl_2(NSOCl)_2}$ were obtained contaminated with a colorless liquid and a white solid from hydrolysis of that portion of the polymeric residue which was soluble in the carbon tetrachloride. This crude product was recrystallized from *n*-hexane, cyclohexane, or *n*-heptane. The purified product had a melting point of 96.5° (uncor) without decomposition. A single crystal examined with a Weissenberg camera employing Cu K$\alpha$ radiation was found to have the lattice parameters of the reported structural determination,[2] and the space group $P2_1/n$ was confirmed; yield, 15% of the theoretical value, based on reacted $\mathrm{NH_2SO_2OH}$.

*Anal.* Calcd for $\mathrm{NPCl_2(NSOCl)_2}$: S, 20.62; P, 9.96; N, 13.51; Cl, 45.60; O, 10.30; mol wt, 310.9. Found: S, 20.67; P, 9.79; N, 13.25; Cl, 45.59; mol wt, 311 (mass spectrometry).

**$\alpha$-$\mathrm{(NSOCl)_3}$ and $\beta$-$\mathrm{(NSOCl)_3}$.**—Samples of these sulfanuric chlorides for nqr measurements were prepared, as described by Vandi, Moeller, and Brown,[4] from pyrolysis of trichlorophosphazosulfonyl chloride and each was identified by comparison of its ir spectrum reported therein. A sample of the $\beta$ form obtained from a separation by vacuum sublimation was used

---

[2] J. C. van de Grampel and A. Vos, *Acta Cryst.*, in press.

[3] A. V. Kirsanov, *J. Gen. Chem. USSR*, **22**, 93 (1952).

[4] A. Vandi, T. Moeller, and T. L. Brown, *Inorg. Chem.*, **2**, 899 (1963).

[5] A. V. Kirsanov, *J. Gen. Chem. USSR*, **22**, 101 (1952).

[6] W. Lehr and M. Becke-Goehring, *Z. Anorg. Allgem. Chem.*, **325**, 287 (1963).

[7] M. Becke-Goehring and W. Lehr, *Chem. Ber.*, **94**, 1591 (1961).

without recrystallization. Samples of the $\alpha$ form were purified by recrystallization from *n*-hexane.

**Infrared Measurements.**—Solution spectra were recorded for the region 4000–420 cm$^{-1}$ on a Perkin-Elmer 337 grating infrared spectrometer using matched KBr cells of 0.1-mm path length. Solid-state spectra were recorded on this instrument and also on a Perkin-Elmer 521 grating infrared spectrometer for the range 4000–244 cm$^{-1}$ using KBr or CsBr pellets or Nujol mulls between KBr or CsBr disks where appropriate. All spectra were obtained using polystyrene film bands for calibration of the wave number scale. Values listed for positions of maximum absorption were reproducible to within 2 cm$^{-1}$.

**Nuclear Quadrupole Interaction Measurements.**—A modified Dean-type externally quenched superregenerative oscillator[8] was employed with phase-sensitive detection and strip chart recording. The frequencies of the interactions were determined by observation of zero beat of the oscillator fundamental with a very loosely coupled BC 221 frequency meter precalibrated against WWV. The interactions have a recorded line width of about 6 kHz at half-height, so with a low level of frequency modulation and by operation in the quasi-incoherent mode it was simple to tune to the line center thereby obtaining the frequency with a reproducibility of ±0.0005 MHz. In this manner the interaction frequencies reproduced the reported Cl quadrupole moment ratio to better than ±0.001%. However, due to the limitation imposed by temperature fluctuations, the reported interactions are presumed to have an accuracy of only ±0.002 MHz. Samples of 0.9–1.9 g sealed under vacuum in glass ampoules were used.

Variation with temperature of the interactions was followed by allowing the sample, in a copper container, to warm. This method is simpler than employing stepwise slush measurements but imprecision in the measured temperature is greater. Temperatures were determined using a copper–constantan thermocouple and a Honeywell portable potentiometer.

## Results and Discussion

The X-ray structural analysis[2] showed that molecules of $NPCl_2(NSOCl)_2$ are in a distorted chair configuration with both sulfur chlorine substituents axial. The most striking feature is the considerable distortion from $C_s$ molecular symmetry resulting from intermolecular interactions between exocyclic atoms. If a mixed-ring molecule possessed $C_s$ symmetry, the chlorines bonded to the sulfur atoms would be chemically equivalent, whereas those bonded to the phosphorus atom would not.

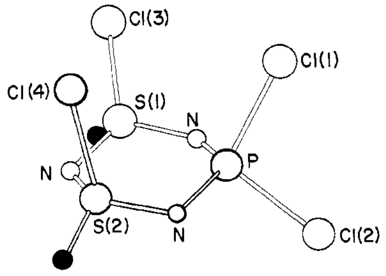

Figure 1.—Molecule of $NPCl_2(NSOCl)_2$. The black solid circles designate oxygen atoms.

**Infrared Data.**—The main bands in the infrared spectra of the mixed ring in the solid state and in solution in polar and nonpolar solvents are listed in Table I. The compound is appreciably soluble in Nujol, the resulting spectrum being that obtained from solution in a nonpolar solvent. Since the spectra obtained from Nujol mulls are thus concentration dependent, this must be taken into account when using the Nujol mull technique to obtain spectra of solid samples. The spectrum in the solid state is very similar to that in polar solvents. However, relative intensities and positions of maximum absorption for certain bands in the solution infrared spectra change gradually with solvent polarity. This variation can be followed from spectra of solutions in mixtures of carbon tetrachloride and acetonitrile as solvent; the over-all change can be seen from a comparison of the solution spectra for nonpolar and polar solvents in Table I.

TABLE I

INFRARED SPECTRA OF $NPCl_2(NSOCl)_2$[a]

| | Soln | |
|---|---|---|
| Solid | Cyclohexane | Acetonitrile |
| 1348 w, sh[b] | 1348 s | 1340 sh |
| 1336 s | 1335 s | 1328 s |
| 1312 w, sh | | 1280 w |
| 1179 vs, br | 1177 vs | 1182 vs |
| 1138 s, br | 1142 s | 1139 s |
| 1028 ms | 1035 m | 1029 s |
| 855 sh | | 915 m |
| 840 m | 840 mw | 841 mw |
| 722 s | 720 ms | 724 ms |
| 666 w | 666 w | 668 w |
| | | 650 w, sh |
| 640 s | 624 s | 635 s |
| 562 s | 558 s | 564 s |
| 548 m | 537 s | 540 m |
| 488 mw | 484 mw | 487 mw |
| 442 w | 437 w | 435 w |
| 410 w | | |
| 348 w | | |
| 310 w | | |

[a] Values (in cm$^{-1}$) of maximum absorption for main bands observed. [b] Abbreviations: vw, very weak; w, weak; mw, medium weak; m, medium; ms, medium strong; s, strong; vs, very strong; sh, shoulder; br, broad. Relative intensities were estimated from absorbance scale.

**Nqr Data.**—The $^{35}Cl$ nuclear quadrupole resonance (nqr) spectra reported in Table II are those observed at room temperature in order to approach the temperatures of the available X-ray structural analysis. The spectrum of the mixed ring consists of four intense interactions of equal magnitude. Four further weaker interactions are attributable to $^{37}Cl$. Considering the $^{35}Cl$ room-temperature nqr spectra of cyclic trimeric phosphonitrilic chloride, $(NPCl_2)_3$, and the $\alpha$ form of sulfanuric chloride, $\alpha$-$(NSOCl)_3$, enables the interactions observed for the mixed ring to be identified with the phosphorus and sulfur chlorine atoms of the molecule. The frequency of the weighted average of the nuclear quadrupole interactions of $(NPCl_2)_3$ is 27.745 MHz. The weighted average of the interactions of $\alpha$-$(NSOCl)_3$ is 36.243 MHz. Thus the lower frequency pair of interactions results from chlorines bonded to the phosphorus atom, and the higher frequency pair of interactions, from chlorines bonded to the two sulfur atoms of the mixed-ring molecules.

The observation of two separate phosphorus chlorine frequencies and also two separate frequencies from the

---

[8] C. Dean and M. Pollack, *Rev. Sci. Instr.*, **29**, 630 (1958).

TABLE II

FREQUENCIES (IN MHz) OF THE $^{35}$Cl NUCLEAR QUADRUPOLE INTERACTIONS OF SOME CYCLIC INORGANIC COMPOUNDS AT 294°K$^a$

| $NPCl_2(NSOCl)_2$ | $\alpha$-$(NSOCl)_3$ | $\beta$-$(NSOCl)_3$$^b$ | $(NPCl_2)_3$$^c$ |
|---|---|---|---|
| 28.660 | 36.138* | 36.134 | 27.880* |
| 29.836 | 36.454 | 36.445 | 27.812 |
| 34.521 | | 37.55 | 27.684 |
| 35.472 | | | 27.608* |

$^a$ All interactions for each compound are of equal intensity except those marked with an asterisk which are of twice the intensity of the others for that compound. $^b$ As the temperature of observation approaches the melting point (320°K), the interactions become less sharp and lose intensity. The highest frequency interaction is particularly affected. $^c$ M. Kaplansky, Ph.D. Thesis, McGill University, 1967.

chemically equivalent sulfur chlorines is in agreement with the solid-state structural determination.[2] The multiplicity of the sulfur chlorine frequencies results from intermolecular interaction reflected in molecular distortion from $C_s$ symmetry.

The frequencies of the respective interactions appear to vary smoothly and exhibit the usual diminution with increasing temperature, implying that no phase transition nor major molecular reorientation occurs within the temperature range studied.

In the process of structural refinement[2] it was found that considerably larger corrections for thermal motion were required for two of the chlorine atoms, Cl(1) and Cl(4), than the corrections calculated using the rigid-body approximation. The temperature dependence of frequencies for molecular crystals has been considered by various authors.[9] At a given temperature, nuclear quadrupole interactions for two chlorine atoms in equivalent bonding situations but otherwise inequivalent environments (*i.e.*, inequivalent nonbonding situations) should be separated by a frequency difference proportional to the relative amount of thermal averaging of the electric field gradient at each nucleus. Contributions to the field gradient, either direct or indirect, from the nonbonded environment, become important only in ionic crystals.[10] The decrease in frequency of interaction with increasing temperature can be accounted for qualitatively by an increase in the amplitude of thermal motion which effects a greater averaging of the electric field gradient at the interacting nucleus. Considering the relative slopes and positions of the plots of nqr frequencies *vs.* temperature for the mixed ring (Figure 2) for the two pairs of interactions, it is possible to relate the higher frequency sulfur–chlorine interaction to Cl(4) and the lower frequency phosphorus–chlorine interaction to Cl(1).

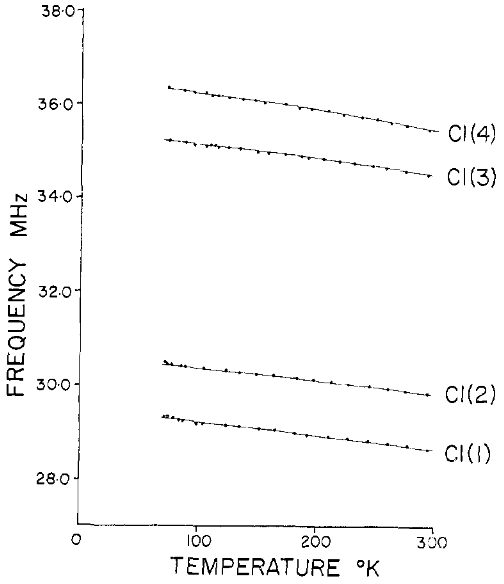

Figure 2.—Temperature dependence of $^{35}$Cl nuclear quadrupole interactions of $NPCl_2(NSOCl)_2$ between the temperature of liquid nitrogen and 294°K.

These assignments will now be discussed in terms of current chemical concepts. The Townes–Dailey theory of nuclear quadrupole coupling considers the major contributions to the electric field gradient within the framework of the LCAO–VB approximation. An increase in chlorine s character and an increase in ionic character of the $\sigma$ bond to a chlorine atom results in a reduction of the frequency of the quadrupolar interaction. Any $\pi$ bonding involving the doubly filled chlorine valence atomic orbitals would reduce the field gradient at the chlorine nucleus thus further reducing the frequency.

To a first approximation the $\sigma$-bond hybrids at either a phosphorus or a sulfur atom in a ring system such as $NPCl_2(NSOCl)_2$ are tetrahedral. The electronegativity of a phosphorus tetrahedral hybrid is lower than that of a sulfur tetrahedral hybrid;[11] hence a phosphorus–chlorine bond would be more ionic than a sulfur–chlorine bond, and the frequency of interaction for phosphorus chlorines would be lower than that of sulfur chlorines. An estimation of the departure from sp$^3$ hybridization at the central atom can be made from a consideration of the determined bond angles. Reduction of the exocyclic angle from 109.4° at a ring phosphorus or sulfur atom reflects a decrease in s character of the central atom exocyclic hybrids. The electronegativity of a hybrid of s and p orbitals decreases with decreasing s character;[11] thus reduction of the exocyclic angle leads to lower $^{35}$Cl nqr frequency. A comparison of the exocyclic angles for $NPCl(NSOCl)_2$, $(NPCl_2)_3$, and $\alpha$-$(NSOCl)_3$ indicates that there are slight differences which may account for the difference in average frequencies for the s and p chlorines. The average ClPCl angle in $(NPCl_2)_3$ is 102°[12] while the ClPCl angle in $NPCl_2(NSOCl)_2$ is 104.4°. The OSCl angles in $\alpha$-$(NSOCl)_3$ and in $NPCl_2(NSOCl)_2$ are 108[13] and 106°, respectively. Thus the interactions for the mixed-

---

(9) (a) H. Bayer, *Z. Physik*, **130**, 227 (1951); (b) T. Kushida, G. B. Benedek, and N. Bloembergen, *Phys. Rev.*, **104**, 1364 (1956); (c) H. D. Stidham, *J. Chem. Phys.*, **49**, 2041 (1968).

(10) R. Ikeda, A. Sasane, D. Nakamura, and M. Kubo, *J. Phys. Chem.*, **70**, 2926 (1966).

(11) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(12) A. Wilson and D. F. Carroll, *J. Chem. Soc.*, 2548 (1960).

(13) A. C. Hazell, G. A. Wiegers, and A. Vos, *Acta Cryst.* **20**, 186 (1966).

ring phosphorus chlorines should occur at a higher average frequency than those observed for $(NPCl_2)_3$ and the interactions for the sulfur chlorines should occur at a lower average frequency than those for $\alpha$-$(NSOCl)_3$; this is observed. It is therefore apparent that a $\sigma$ bond inductive effect is present.

The endocyclic bonding in such cyclic inorganic compounds is complex and has recently been described by Mitchell.[14,15] It is characterized by $\pi$ and $\pi'$ systems in addition to the $\sigma$ bonding. Exocyclic $\pi$ bonding (discussed subsequently) will be in competition with the $\pi$ and $\pi'$ systems. Evaluation of the magnitude of the asymmetry parameter at the Cl atom is unlikely to yield further information on the bonding as both the Cl lone-pair orbitals can become involved in the exocyclic $\pi$ bonding according to symmetry considerations.

The $^{35}Cl$ nqr spectrum of $\alpha$-$(NSOCl)_3$ shows a single interaction and another half as intense separated by 0.316 MHz. This is in agreement with the solid-state structural determination[13] which places two-thirds of the chlorine atoms per unit cell in different crystallographic sites from the remaining third although all chlorine atoms are chemically equivalent. The $^{35}Cl$ nqr spectrum of $\beta$-$(NSOCl)_3$, Table II, shows three interactions of equal intensity; two are closely spaced and the third is much further removed. It is thus consistent with the suggestion of Vandi, Moeller, and Brown,[4] inferred from dipole moment studies, that the molecular configuration is chair with two chlorines axial and one chlorine equatorial.

The frequency separations of both pairs of interactions in the mixed ring are large compared with those of $\alpha$-$(NSOCl)_3$ and $(NPCl_2)_3$ or $(NPCl_2)_4$.[16,17] In solid-state $NPCl_2(NSOCl)_2$ there is a significant difference in the sulfur–chlorine interatomic distances (S(1)–Cl(3), 2.007 Å; S(2)–Cl(4), 2.028 Å) due to a distorted $C_s$ symmetry. The $^{35}Cl$ coupling constant increases with increasing bond length for covalent bonds due to a decrease in the chlorine $\sigma$-bond s and ionic characters.[18] This effect is considerable for a carbon–chlorine bond and can account for the separation observed between the sulfur–chlorine interactions.

The phosphorus–chlorine interatomic distances are identical within the limits of error. Dixon, *et al.*,[17] have assigned the interactions observed for the two known forms of $(NPCl_2)_4$ on the basis of varying amounts of exocyclic $\pi$ bonding estimated from the "polar" angle between the exocyclic bond and the direction perpendicular to the plane of the ring segment NPN. The angle determines the amount of overlap between occupied chlorine p orbitals and suitably oriented unoccupied phosphorus d orbitals. For example, "polar" angles calculated for the chair form[19] of $(NPCl_2)_4$ are: Cl(1), 43.9°; Cl(2), 32.8°; Cl(3), 40.4°; Cl(4), 37.0°. The room-temperature interaction frequencies (in MHz) can be assigned as 27.224, 28.597, 28.093, and 28.150, respectively.[16] The "polar" angles for the mixed-ring phosphorus chlorines are: Cl(1), 39.0°; Cl(2), 36.0°. The assigned frequencies are 28.660 and 29.836 MHz, respectively. Any $\pi$ effect is thus in the correct direction to explain the separation. However, in $(NPCl_2)_4$ for example, separations of 1.373 and 0.057 MHz are related to "polar" angle differences of 11.0 and 3.1°, while the separation of 1.786 MHz must be related to an angle difference of 3.0°. The relative positions of the interactions for $\alpha$-$(NSOCl)_3$ cannot be accounted for by invoking similar $\pi$ bonding involving the chlorine atoms. As has been noted, these interactions can be assigned unambiguously from the intensity ratios. The "polar" angles calculated for $\alpha$-$(NSOCl)_3$ (Cl(1), 30.1°; Cl(2), 31.4°) would place the interactions in the reverse order to that observed. Therefore the effect, if it occurs, must be masked by some opposing effect.

Such chemically equivalent groups of chlorines would have differences in thermal averaging of their electric field gradients reflecting crystal-packing effects. A measure of mean-square amplitude of vibration, $\overline{u^2}$, in a given direction for an atom can be determined from the anisotropic thermal parameters, $U_{ij}$, found from a structural refinement according to Cruickshank[20]

$$\overline{u^2} = \sum_i \sum_j U_{ij} l_i l_j$$

$\mathbf{l} = l_i, l_j, l_k$ is a unit vector defining the direction of vibration. Choosing directions of vibration along the bond to a particular chlorine atom, perpendicular to the plane defined by the exocyclic substituents and the atom to which they are bonded and perpendicular to the bond to the chlorine in this plane, values of $\overline{u^2}$ for each chlorine atom were determined. A qualitative comparison of the "net motion" of each chlorine atom with respect to that of the atom to which it is bonded in the same directions leads to the conclusion that the thermal motion of Cl(1) is greater than that of Cl(2) for $NPCl_2(NSOCl)_2$. From similar calculations for $(NPCl_2)_4$ and $\alpha$-$(NSOCl)_3$ based on the $U_{ij}$ values reported for the structural refinements,[12,19] the observed nqr interactions can be assigned to particular chlorine atoms. For $(NPCl_2)_4$, the assignment and relative separations fall in the same pattern as that based on the $\pi$ effect.[17] In addition, the separation and relative position of the two interactions observed for the crystallographically inequivalent chlorines of $\alpha$-$(NSOCl)_3$ can be explained on this basis.

Thus, both a $\pi$ effect and consideration of relative thermal averaging fit the assignment of phosphorus–chlorine interactions, while the $\pi$ effect alone cannot explain the assignment for the sulfur chlorines in these ring compounds.

It must be noted that relative thermal averaging calculated for Cl(3) and Cl(4) of $NPCl_2(NSOCl)_2$

---

(14) K. A. R. Mitchell, *J. Chem. Soc.*, *A*, 2683 (1968).

(15) K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

(16) M. Kaplansky, Ph.D. Thesis, McGill University, 1967.

(17) M. Dixon, H. D. E. Jenkins, J. A. S. Smith, and D. A. Tong, *Trans. Faraday Soc.*, **63**, 2853 (1967).

(18) J. Duchesne, *J. Chem. Phys.*, **20**, 1804 (1952).

(19) A. J. Wagner and A. Vos, *Acta Cryst.*, **B24**, 707 (1968).

(20) D. W. J. Cruickshank, *ibid.*, **9**, 749, 754 (1956).

would position the interactions assigned to these chlorines in the reverse order, inplying that the difference in bond lengths in this case is of much greater importance in determining interaction frequencies.[21,22]

**Acknowledgment.**—The authors wish to acknowledge with gratitude the generous cooperation of Dr. Aafje Vos in providing them with the X-ray structural analysis prior to publication. This research was supported by the Defense Research Board of Canada, Grant No. DRB-9530-55, and by the National Research Council of Canada to which R. C. is indebted for studentships, 1966–1968.

(21) An alternative approach to the assignment of the lower frequency pair of interactions was suggested by a referee: Cl(1) and Cl(2), having different crystallographic environments, have different average moments of inertia with respect to the principal direction of their field gradient tensors and hence different temperature dependences of their electric field gradients and nqr frequencies. Using the moments of inertia and a detailed calculation on an assembly of quantum mechanical harmonic oscillators the zero-point vibrational contribution to the electric field gradient could be separated out. This was attempted by Ragle[22] using a value for the restoring force constant for 1,2-dichloroethane, a simple and relatively well-understood molecule, and found to be about 1.2% of the value of the coupling constant. For Cl(1) and Cl(2) the splitting amounts to about 3.6% of the average of the estimated coupling constants and it is unlikely that the difference in their respective zero-point vibrational contributions could even approach 3.6%; thus this alternative approach would not reverse the assignments. Further calculation is not possible without knowledge of the restoring forces in the molecule.

(22) J. L. Ragle, *J. Phys. Chem.*, **63**, 1395 (1959).

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

# Difluorothiophosphoryl-$\mu$-thio-difluorophosphine and Difluorophosphoryl-$\mu$-oxo-difluorophosphine. Novel Mixed-Valence Fluorophosphorus Compounds[1]

BY T. L. CHARLTON AND R. G. CAVELL

*Received April 7, 1969*

The compound $F_4P_2S_2$, a moderately stable volatile liquid (bp 85.7°), has been prepared by the reaction of iodothiophosphoryl difluoride with a stoichiometric quantity of mercury and by the reaction of difluorodithiophosphoric acid with dimethylaminodifluorophosphine. The reaction of difluorophosphoric acid with dimethylaminodifluorophosphine gives the considerably less stable oxygen analog $F_4P_2O_2$ (bp 50°). Infrared and nuclear magnetic resonance spectral measurements and chemical studies indicate that the compounds do not have a phosphorus–phosphorus bonded structure but rather the isomeric structure $F_2P({=}E)EPF_2$ ($E = S, O$) with trivalent and pentavalent phosphorus linked by a sulfur- or an oxygen-bridging atom.

## Introduction

Many diphosphorus compounds containing a phosphorus–phosphorus bond have been synthesized by coupling halogenophosphorus monomers with active metals.[2–4] We now wish to report successful synthesis of diphosphorus compounds derived from phosphoryl and thiophosphoryl difluoride monomers. These compounds, however, do not possess the phosphorus–phosphorus bonded structure.

## Experimental Section

Standard vacuum techniques using Pyrex-glass apparatus were employed throughout. Stopcocks were lubricated with Apiezon N grease. Infrared spectra were measured with a Perkin-Elmer 421 (4000–300 cm$^{-1}$) dual-grating instrument, mass spectra with an AEI MS-9 double-focusing mass spectrometer, and nuclear magnetic resonance spectra with Varian A 56/60 or HA 100 instruments. All fluorine spectra were measured on 10% solutions of compounds in $CCl_3F$ at 56.4 MHz with chemical shifts given relative to $CCl_3F$. Phosphorus spectra were measured on neat samples at 40.5 MHz with chemical shifts given relative to $P_4O_6$[5] which was contained within a reference capillary in the sample.

**Preparation of Difluorothiophosphoryl-$\mu$-thio-difluorophosphine. (a) From Iodothiophosphoryl Difluoride and Mercury.**—In a typical experiment, $SPF_2I$[6] (1.16 g, 5.10 mmol) and a stoichiometric quantity of mercury (0.51 g, 2.56 mmol) were sealed in a 75-cm$^3$ reaction tube which was vigorously shaken for 1 week at room temperature. Separation of the volatile products gave $F_4P_2S_2$ (0.49 g, 2.42 mmol, 95% yield based on eq 3) collected at −81°, $SPF_2H$[7] (0.018 g, 0.176 mmol) condensed at −116°, and a trace of $(SPF_2)_2S$[8] condensed at −65°. The reaction vessel contained mercuric iodide (1.08 g, 2.38 mmol).

**(b) From Difluorodithiophosphoric Acid and Dimethylaminodifluorophosphine.**—$F_2P(S)SH$[9] (1.00 g, 7.50 mmol) and $F_2PN(CH_3)_2$[10] (0.465 g, 4.11 mmol) reacted immediately upon warming to room temperature in a 75-cm$^3$ tube to form a white solid and a volatile liquid. Separation of the volatile products after 15 min of reaction at room temperature gave $F_2PSP(S)F_2$ (0.72 g, 3.57 mmol, 95% yield based on eq 4) collected at −81° and a mixture of $PF_3$ and $PF_2N(CH_3)_2$ (0.05 g) collected at −196°. A solution of the residual white solid in $CH_3CN$ gave $^1H$ and $^{19}F$ nmr lines corresponding to[11] $(CH_3)_2NH_2{}^+S_2PF_2{}^-$.

**Characterization of Difluorothiophosphoryl-$\mu$-thio-difluorophosphine.**—$F_2PSP(S)F_2$ was a clear, colorless liquid which was characterized by spectroscopic studies, by vapor density molecular

---

(1) For a preliminary communication see R. G. Cavell, T. L. Charlton, and A. A. Pinkerton, *Chem. Commun.*, 424 (1969).

(2) A. H. Cowley, *Chem. Rev.*, **65**, 617 (1965).

(3) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966).

(4) M. Lustig, J. K. Ruff, and C. B. Colburn, *ibid.*, **88**, 3875 (1966).

(5) A. C. Chapman, J. Homer, D. J. Mowthorpe, and R. T. Jones, *Chem. Commun.*, 121 (1965).

(6) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **7**, 2195 (1968). A typographical error in Table III of this paper gives the fluorine chemical shift of $SPF_2I$ as +11.2 ppm *vs.* $CCl_3F$. It should be −11.2 ppm.

(7) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **6**, 2204 (1967).

(8) T. L. Charlton and R. G. Cavell, unpublished results.

(9) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 281 (1969); R. W. Mitchell, M. Lustig, F. A. Hartmann, J. K. Ruff, and J. A. Merritt, *J. Am. Chem. Soc.*, **90**, 6329 (1968).

(10) R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).

(11) R. G. Cavell, *Can. J. Chem.*, **46**, 613 (1968).