

TABLE IV
 COMPARISON OF SEVERAL BOND DISTANCES (Å)

Compounds	C(5)- C(6)	C(6)- N(2)	Ni- N(1)	Ni- N(2)
Bis(pyridine-2-carboxamido)- nickel(II) dihydrate				
This research	1.51	1.32	1.92	1.87
Ref 7	1.47	1.27	1.93	1.95
Diaquobis(pyridine-2-carbox- amide)nickel(II) chloride ^a	1.50	1.31	2.02	
Picolinamide ^b	1.51	1.33		
Amino acids, simple peptides, and related compounds ^c	1.53	1.32		

^a A. Masuko, T. Nomura, and Y. Saito, *Bull. Chem. Soc. Japan*, **40**, 511 (1967). ^b See ref 15. ^c L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1967, p 163.

the lattice points of a structure register the lattice points of the reversed structure. Twinning is most likely to occur according to Mallard's empirical theory.¹⁶ The question as to whether β is exactly 90° is not answered here because of the limitation of our instrument.

(16) M. J. Buerger, "Crystal Structure Analysis," John Wiley & Sons, Inc., New York, N. Y., 1967, pp 53-76.

Comments on the Paper of Nawata, *et al.*

After the completion of the structure analysis of bis-(pyridine-2-carboxamido)nickel(II) dihydrate, we noticed a paper by Nawata, *et al.*,⁷ on crystal structure of the same compound, prepared according to the method of Yamasaki and Sekizaki,¹⁷ with a final R factor of 0.160. By adopting a microscopic incoherent twinning model, we obtained a final R factor of 0.107. A comparison of several bond distances is given in Table IV. Our results indicate that coordination with nickel(II) does not affect the C(5)-C(6) and C(6)-N(2) bond distances.

Acknowledgments.—We thank Professor G. A. Jeffrey for permission to use his laboratory at the University of Pittsburgh for taking the X-ray intensity data and Dr. R. D. Rosenstein for help during data collection. Dr. W. R. Busing of Oak Ridge National Laboratory and Dr. R. Shiono of the University of Pittsburgh kindly provided us with versions of least-squares refinement programs. Mr. J. R. Hayes of Duquesne University helped in adapting programs to the computer system at Duquesne University.

(17) K. Yamasaki and M. Sekizaki, *Bull. Chem. Soc. Japan*, **38**, 2206 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND MATERIALS RESEARCH LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Structural and Spectroscopic Studies of Tetrachlorophosphonium Tetrachloroferrate(III), $[\text{PCl}_4][\text{FeCl}_4]$ ^{1a}

BY T. J. KISTENMACHER^{1b} AND G. D. STUCKY

Received May 10, 1968

The crystal and molecular structure of tetrachlorophosphonium tetrachloroferrate(III), $[\text{PCl}_4][\text{FeCl}_4]$, has been determined by three-dimensional X-ray data collected by counter methods. Full-matrix least-squares refinement on 1590 reflections gave a final R factor of 2.7% based on F . The crystal system is orthorhombic with the possible space groups D_{2h}^{11} -Pbcm or C_{2v}^5 -Pbc2₁. The cell constants are $a = 6.231$, $b = 13.479$, $c = 14.078$ Å, with $Z = 4$. The calculated density of 2.08 g/cm³ agrees well with the observed density of 2.09 ± 0.02 g/cm³. The structure consists of isolated, nearly tetrahedral PCl_4^+ and FeCl_4^- units. The effects on the bond distances due to thermal motion are considered. Results of infrared and optical spectral studies are also reported.

I. Introduction

The syntheses of many phosphorus pentahalide-metal trichloride complexes have been reported.² In most cases, the resulting complex has been postulated to be composed of the tetrachlorophosphonium cation and the tetrachlorometalate anion. The existence of the tetrachlorophosphonium cation has been crystallographically confirmed only in phosphorus pentachloride³ itself. There are also few structural^{4,5} and

spectroscopic⁶⁻¹⁰ data available on four-coordinate iron(III). In view of the above considerations and as part of an extended study of metal halide systems, the X-ray structure and spectral properties of $[\text{PCl}_4][\text{FeCl}_4]$ have been determined and are reported here.

II. Experimental Section

Crystals of $[\text{PCl}_4][\text{FeCl}_4]$ were prepared by the method of Groeneveld.² A typical preparation involved the mixing of a solution of anhydrous FeCl_3 in thionyl chloride (with a small

(1) (a) This work was supported in part by the Advanced Research Projects Agency under Contract SD-131; (b) Mobil Oil Corp. predoctoral fellow.

(2) W. L. Groeneveld, *Rec. Trav. Chim.*, **71**, 1152 (1952).

(3) D. Clark, H. M. Powell, and A. F. Wells, *J. Chem. Soc.*, 642 (1942).

(4) (a) B. Zaslav and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957); (b) R. R. Richards and N. W. Gregory, *ibid.*, **69**, 239 (1965).

(5) M. J. Bennett, F. A. Cotton, and D. L. Weaver, *Acta Cryst.*, **23**, 581 (1967).

(6) H. L. Friedman, *J. Am. Chem. Soc.*, **84**, 167 (1962).

(7) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, London, 1962.

(8) A. P. Ginsberg, and M. B. Robin, *Inorg. Chem.*, **2**, 817 (1963).

(9) C. K. Jørgensen, "Structure and Bonding," Vol. I, Springer-Verlag, New York, N. Y., 1966, pp 3-31.

(10) S. Balt, *Rec. Trav. Chim.*, **86**, 1025 (1967).

amount of phosphorus oxychloride added to increase the solubility of the FeCl_3 with a solution of PCl_3 in thionyl chloride. The solution was initially deep red and gradually changed to a yellow-brown. The preparation was performed in a modified Schlenk-tube apparatus and at all times care was taken to eliminate contamination by water. After a period of 1 week to 10 days, bright yellow crystals formed in the tube. The complex itself is extremely water sensitive and all further manipulations were carried out in a drybox under an argon atmosphere.

Anal. Calcd for PFeCl_8 : P, 8.4; Fe, 15.1; Cl, 76.6. Found: Fe, 15.1; Cl, 76.3.

The compound shows two crystal habits: assorted polyhedra (mostly truncated or full octahedra) and well-formed rods which to within about 5% were cylindrical in cross section. Both forms were shown to be crystallographically equivalent by X-ray investigations.

Infrared measurements were made on Beckman Model IR5A and Perkin-Elmer Model 521 spectrophotometers. In the region 700–4000 cm^{-1} NaCl optics were used; in the region 300–900 cm^{-1} CsBr optics were used. Samples were milled in Nujol and prepared in a drybox under argon atmosphere. Even when the samples were protected by the Nujol film, hydrolysis was a severe problem.

The electronic absorption spectra were recorded on a Cary model 14RI spectrophotometer. Several different methods of preserving the water-sensitive crystals were employed. None of the methods gave satisfactory results at low temperatures (77°K) owing to cracking and clouding of the crystal. However, the spectral results at room temperature were very consistent for many differently shaped crystals and coating techniques. The experimental results were obtained on a crystal approximately 1.1 mm thick which was coated with a thin film of Kel-F grease and placed in an optical dewar under a nitrogen flow. The surface of the crystal showed slight striations and was not of uniform thickness, so the extinction coefficients reported are of an approximate nature ($\pm 0.2 \text{ mol}^{-1} \text{ l. cm}^{-1}$). The error limits on the experimental frequencies are approximately $\pm 70 \text{ cm}^{-1}$.

III. Collection and Reduction of the Intensity Data

An optical study indicated that the crystals were biaxial and monochroic. X-Ray investigation showed the crystal system to be orthorhombic. Systematic absences as determined by precession and Weissenberg photographs were: $0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$. These absences are consistent with the orthorhombic space groups: D_{2h}^{11} -Pbcm (centric) and C_{2v}^5 -Pbc2₁ (acentric). Lattice constants and standard deviations obtained by a least-squares refinement¹¹ of the angular settings of 14 reflections which were carefully centered on a Picker four-circle diffractometer are: $a = 6.231 \pm 0.001 \text{ \AA}$, $b = 13.479 \pm 0.003 \text{ \AA}$, $c = 14.078 \pm 0.003 \text{ \AA}$, and $V = 1182.37 \text{ \AA}^3$ (28° ; $\lambda(\text{Mo K}\alpha) 0.71069 \text{ \AA}$).

The calculated density of 2.08 g/cm^3 for four molecules per unit cell agrees well with the observed density of $2.09 \pm 0.02 \text{ g/cm}^3$ measured by flotation methods in a mixture of methylene iodide, chlorobenzene, and bromobenzene. The centrosymmetric space group, Pbcm, requires the P or Fe atoms to occupy sites with mirror, twofold, or inversion symmetry. The noncentrosymmetric space group, Pbc2₁, places no symmetry requirements on the positioning of the P or Fe atoms.

All of the crystals with the polyhedral habit, but none of the rodlike modification, showed twinning under optical study in crossed polarized light or X-ray examination. Accordingly, a rod, approximated as a cylinder

0.85 mm in length and 0.40 mm in diameter, was mounted along [100] in a glass capillary. The X-ray intensity measurements were made with Mo $\text{K}\alpha$ radiation (calculated linear absorption coefficient, $\mu = 31.9 \text{ cm}^{-1}$) because of the large absorption correction with Cu $\text{K}\alpha$ radiation ($\mu = 280.1 \text{ cm}^{-1}$). Even though the crystal chosen for the X-ray study was fairly large, the mosaic spread as determined by an ω -scan technique over several peaks in various 2θ ranges was 0.08° . The intensities were measured with a scintillation counter mounted 21 cm from the crystal. Intensity data were collected up to 60° in 2θ . Below 30° a symmetrical scan of 1° was taken about the position calculated for $\text{K}\alpha_1$; above 30° the scan was from -0.60° below the value calculated for $\text{K}\alpha_1$ to $+0.73^\circ$ above the calculated position. Stationary background counts of 20 sec were taken at the beginning and at the end of the scan. The diffracted beams were collected by a 1.0-mm collimator and filtered through 0.0005-in. zirconium foil before entering the counter tube. No additional attenuation was applied to the diffracted beam as all intensities were found to lie within the linear response range of the electronics of the detector system. The intensities were collected by the θ - 2θ scan technique with a takeoff angle of 0.8° and a scan rate of 1° min^{-1} . Two symmetry-related forms, hkl and $\bar{h}kl$, were collected because their equivalence is not affected by anomalous dispersion effects¹² for either Pbcm (point group mmm) or Pbc2₁ (point group mm2). A total of 3640 reflections (including a check on the required extinctions) were collected. The intensities were corrected for Lorentz-polarization and absorption (with the cylindrical dimensions given above).¹³ An estimation of the standard deviations, $\sigma(F)$, of the structure factors derived from intensities (I) corrected for background is given by

$$\sigma(|F|) = \frac{|F|}{2I} [\text{CN} + 0.25(\text{TC}/\text{TB})^2(B_1 + B_2) + p^2I^2]^{1/2}$$

where CN is the total integrated peak counts in a scan of time TC, and B_1 and B_2 are the background counts in a time TB. The factor p was taken to be 0.01. A more complete discussion of this type of empirical estimation of the standard deviations has recently been given by Ibers.^{14,15} The weighting scheme used in the refinement was based on $1/\sigma(F)^2$. Unobserved reflections ($I_o < 3\sigma(I)$) were given a raw intensity of $\sigma(I)^{16}$ and assigned a standard deviation of $2I_{\text{min}}/\sqrt{45}$, where $I_{\text{min}} = 3\sigma(I)$.¹⁶ Twenty-two peaks for which $I_o < (I_{\text{BKG}} - 3\sigma(I_{\text{BKG}}))$ were rejected. During the refinement unobserved reflections with $F_o > F_c$ were given a weight of zero. The scattering factors for all atoms were taken from the compilation of Hanson, Herman, Lea, and Skillman.¹⁷ Anomalous dispersion correc-

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(13) L. J. Guggenberger and C. Prewitt, "Program ACAC," E. I. du Pont de Nemours and Co., Wilmington, Del., 1966.

(14) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(15) R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 205 (1967).

(16) W. C. Hamilton, *Acta Cryst.*, **8**, 185 (1955).

(17) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *ibid.*, **17**, 1040 (1964).

(11) J. Gvildys and M. Mueller, "B-101, Orientation and Angle Setting Generation Program," Argonne National Laboratory, Argonne, Ill., 1965.

TABLE I
 POSITIONAL AND THERMAL PARAMETERS FOR $[\text{PCL}_4][\text{FeCl}_4]$

Atom	x	y	z	B_{11}^a	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0.2720 (1) ^b	0.0268 (1)	0.2500	0.0169 (2)	0.0053 (1)	0.0040 (1)	-0.0001 (1)	0.000	0.0000
Cl(1)	0.4030 (1)	-0.0380 (1)	0.1203 (1)	0.0290 (3)	0.0123 (1)	0.0067 (1)	-0.0003 (2)	0.0027 (1)	-0.0037 (1)
Cl(2)	0.3361 (2)	0.1863 (1)	0.2500	0.0394 (5)	0.0054 (1)	0.0104 (1)	-0.0024 (2)	0.0000	0.0000
Cl(3)	-0.0753 (2)	0.0034 (1)	0.2500	0.0174 (4)	0.0085 (1)	0.0074 (1)	-0.0008 (2)	0.0000	0.0000
P	-0.0453 (2)	0.2500	0.0000	0.0226 (4)	0.0053 (1)	0.0047 (1)	0.0000	0.0000	0.0003 (1)
Cl(4)	0.1344 (2)	0.3529 (1)	0.0490 (1)	0.0376 (3)	0.0082 (1)	0.0135 (1)	-0.0043 (1)	-0.0016 (2)	-0.0004 (1)
Cl(5)	-0.2240 (2)	0.1977 (1)	0.0974 (1)	0.0483 (4)	0.0129 (1)	0.0077 (1)	-0.0032 (2)	0.0049 (2)	0.0037 (1)

^a The form of the anisotropic ellipsoid is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. ^b Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits.

tions ($\Delta f'$ and $\Delta f''$) for P, Cl, and Fe were taken from Table 3.3.2c of the "International Tables for X-Ray Crystallography" (Vol. III, 1962) and applied to the calculated structure factors.

IV. Solution and Refinement of the Structure

A three-dimensional Patterson function¹⁸ was calculated using the 696 observed reflections of the hkl form. The distribution of peaks on the Patterson map was most consistent with the centrosymmetric space group Pbcm. In conjunction with the spectral results to be discussed later, the most probable positions of the Fe atom in the space group Pbcm are: Wyckoff set 4(d), mirror symmetry; Wyckoff set 4(c), twofold symmetry.

The Patterson map was compatible with the Fe atom positioned in set 4(d) with $x = 0.26$, $y = 0.03$, $z = 0.25$. Subsequent Fourier¹⁸ syntheses gave the positions of the phosphorus and the five chlorine atoms. The P atom lies in the special position 4(c) of Pbcm. Two of the chlorines (Cl(2) and Cl(3)) lie in the set 4(d). The other three chlorines (Cl(1), Cl(4), and Cl(5)) are in general positions. Three cycles of least-squares¹⁹ refinement on the one scale factor and the positional parameters gave $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma F_o = 0.211$. Three further cycles of refinement in which the isotropic temperature factors were allowed to vary gave $R_1 = 0.134$ for the 696 observed reflections with positive hkl indices. At this point, the two sets of symmetry-related data were averaged to give a total of 1590 reflections of which 850 were judged to be unobserved. The weighting scheme described previously was applied to all reflections. Two cycles of isotropic refinement on the averaged data set gave $R_1 = 0.125$ and $R_2 = (\Sigma w \cdot (F_o - F_c)^2 / \Sigma w F_o^2)^{1/2} = 0.107$. Calculations of anisotropic thermal parameters for all atoms and four subsequent least-squares refinements on the one scale factor and the positional and thermal parameters (51 total parameters) gave as final discrepancy indices $R_1 = 0.042$ (observed data) and $R_2 = 0.027$ (observed and unobserved data). A final difference Fourier map showed no peaks higher than $0.6 \text{ e}^-/\text{\AA}^3$. The estimated standard deviation of an observation of unit weight is 1.56. The value of $w(F_o - F_c)$ shows no significant

(18) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "A Two- and Three-Dimensional Fourier Program for the IBM 709/7090, *PRFR-2*, 1962.

(19) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," U. S. Atomic Energy Commission Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

systematic variation with the magnitude of the structure factors or $(\sin \theta)/\lambda$. The positional and thermal parameters derived from the last cycle of least-squares refinement are presented in Table I, along with the standard deviations in these parameters. A partial summary of bond distances and angles and their errors²⁰ appears in Table II. The observed and calculated

 TABLE II
 SELECTED BOND DISTANCES (Å) AND ANGLES (DEG)^a

Boned distances		Near-neighbor distances between ions	
Fe-Cl(1)	2.1819 (10)	Fe-P	5.0348 (10)
Fe-Cl(2)	2.1873 (15)	Cl(1)-Cl(4)	5.6196 (20)
Fe-Cl(3)	2.1869 (14)	Cl(2)-Cl(4)	3.8248 (17)
P-Cl(4)	1.9123 (12)	Cl(3)-Cl(4)	5.6496 (19)
P-Cl(5)	1.9024 (13)	Cl(1)-Cl(5)	5.0453 (17)
		Cl(2)-Cl(5)	4.1005 (18)
		Cl(3)-Cl(5)	3.5113 (15)
Bond angles ^b		Near-neighbor distances within an ion	
Cl(1)-Fe-Cl(2)	108.98 (4)	Cl(1)-Cl(2)	3.5566 (16)
Cl(1)-Fe-Cl(3)	108.20 (4)	Cl(1)-Cl(3)	3.5389 (15)
Cl(2)-Fe-Cl(3)	108.83 (6)	Cl(2)-Cl(3)	3.5572 (19)
Cl(1)-Fe-Cl(1)'	113.56 (6)	Cl(1)-Cl(1)'	3.6506 (22)
Cl(4)-P-Cl(5)	110.58 (5)	Cl(4)-Cl(5)	3.1359 (16)
Cl(4)-P-Cl(5)'	109.50 (5)	Cl(4)-Cl(4)'	3.1000 (21)
Cl(4)-P-Cl(4)'	108.30 (5)	Cl(5)-Cl(5)'	3.0857 (22)
Cl(5)-P-Cl(5)'	108.38 (6)	Cl(4)-Cl(5)'	3.1153 (17)

^a Errors in the lattice parameters are included in the estimated standard deviations. ^b Symmetry-related atoms are indicated by the prime after the atom designation.

structure factors for the 1590 reflections of the symmetry-averaged data set are given in Table III. Table IV is a collection of the root-mean-square displacements for all atoms. Figures 1 and 2 show the inner coordination sphere around the iron and the phosphorus. Figure 3 is a perspective view of the packing in the unit cell. The drawings were made with the aid of Johnson's computer program.²¹

In an attempt to resolve the space group ambiguity, statistical tests²² were run on the Mo $K\alpha$ data, and a set of Cu $K\alpha$ data was collected. The results of the statistical tests were inconclusive, but favored the acentric space group. The Cu $K\alpha$ data were collected because of the large anomalous dispersion effects of Fe and

(20) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," U. S. Atomic Energy Commission Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(21) C. K. Johnson, "ORTEP, a Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," U. S. Atomic Energy Commission Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(22) B. K. Dewar, A. L. Stone, and E. B. Fleischer, "Program FAMR," private communication.

TABLE III
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR [PCl4][FeCl4]2

Table with columns for h, k, l, F_obs, F_calc, and various Miller indices (hkl). It lists observed and calculated structure factors for the compound [PCl4][FeCl4]2.

Unobserved reflections are indicated with an asterisk. OBS = F_o/scale factor; scale factor = 0.20585 (26); F(000) = 612.1.

Cl atoms with this radiation. A total of 204 reflections were collected on a Picker four-circle diffractometer, and 102 reflections were collected in each of the forms hkl and hkl. For the point group mm2 (Pbc21), these two forms are nonequivalent, while for the point group mmm (Pbcm), they are properly equivalent forms. No systematic variation in the intensities of the two forms was discernible. The rather low R factor for the refinement in the centric space group also favors Pbcm as the correct choice. In any case, the refinement in the centric space group seems to indicate that, if the true space group is the acentric one, deviations from centrosymmetry must be very small and perhaps within the standard deviations reported here.

V. Discussion

The spectra of the PCl4+ ion in both the infrared and Raman regions have been previously reported. The Raman spectrum of FeCl4- has also been re-

TABLE IV
ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)
ALONG THE PRINCIPAL AXES R^a

Table with columns for Atom, R1, R2, and R3. It lists root-mean-square amplitudes of vibration along the principal axes for Fe, Cl(1), Cl(2), Cl(3), Cl(4), and Cl(5).

See Figures 1 and 2.

ported. Table V gives a comparison between the infrared spectrum of PAICl3 reported by Carlson and that of [PCl4][FeCl4] reported here. The close cor-

- (23) H. Gerding and H. Houtgraaf, Rec. Trav. Chim., 72, 21 (1953).
(24) T. C. Waddington and F. Klanberg, J. Chem. Soc., 2339 (1960).
(25) I. R. Beattie and M. Webster, ibid., 38 (1963).
(26) V. P. Petro and S. G. Shore, ibid., 336 (1964).
(27) G. L. Carlson, Spectrochim. Acta, 19, 1291 (1963).
(28) L. A. Woodward and M. S. Taylor, J. Chem. Soc., 4473 (1960).

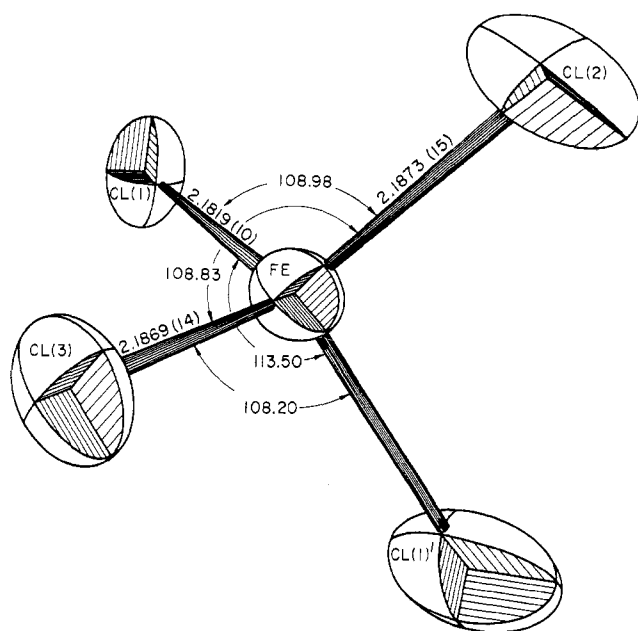


Figure 1.—Inner coordination about the iron. The mirror at $Z = 1/4$ contains the Fe, Cl(2), and Cl(3) atoms.

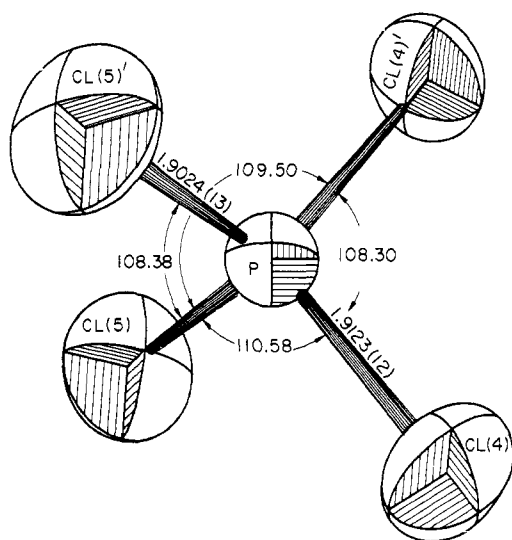


Figure 2.—Inner coordination about the phosphorus.

correspondence between the bands assigned to PCl_4^+ in $[\text{PCl}_4][\text{FeCl}_4]$ and those of PAICl_3 tends to confirm Carlson's postulate that PAICl_3 consists of PCl_4^+ and AlCl_4^- ions in the solid state. The band at 376 cm^{-1} has been assigned to the $\nu_3(\text{F}_2)$ band of FeCl_4^- in correspondence with the study of Woodward and Taylor²⁸ on the extraction of FeCl_3 from an aqueous HCl solution into ether. In freshly prepared samples, the band at 580 cm^{-1} is absent or very weak but grows very rapidly with time and has been assigned to the $\nu_4(\text{E})$ band of POCl_3 .²⁹ Table VI gives the results of the single-crystal electronic spectra. The molar extinction coefficients are slightly higher than those reported for analogous bands in the solution spectra of tetraethylammonium tetrachloroferrate(III) in acetone.¹⁰ An attempt was made to assign the electronic spectrum on the basis

(29) M. L. Delwaille and F. Francois, *Compt. Rend.*, **220**, 817 (1945).

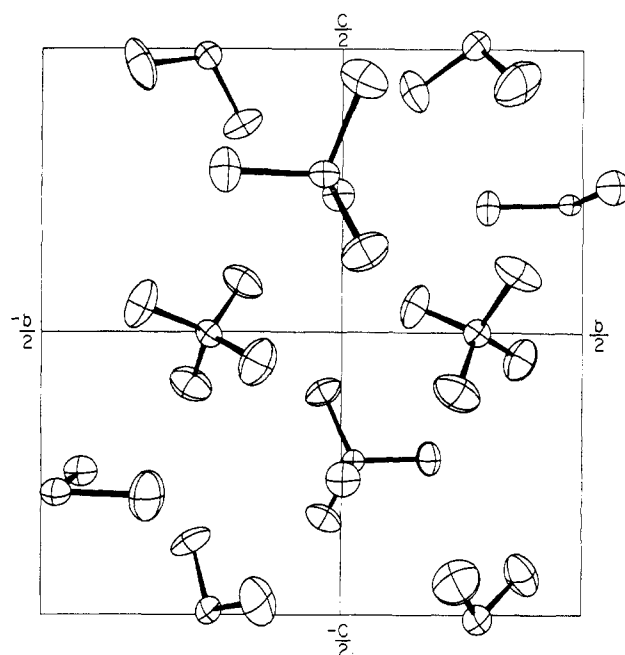


Figure 3.—A perspective view perpendicular to the bc plane.

TABLE V
INFRARED INTENSITY DATA

Band, cm^{-1}	— PAICl_3 (Carlson ²⁷)—		— $[\text{PCl}_4][\text{FeCl}_4]$ (this work)	
	Intens ^a	Assignment ^b	Band, cm^{-1}	Intens
180	s	$\nu_4(\text{F}_2)(\text{AlCl}_4^-)$		
253	s	$\nu_4(\text{F}_2)(\text{PCl}_4^+)$		
347	vw	$\nu_1(\text{A}_1)(\text{AlCl}_4^-)$	376 ^c	vs, br
430	vw, sh	$\nu_4 + \nu_2(\text{PCl}_4^+)$		
490	vs	$\nu_3(\text{F}_2)(\text{AlCl}_4^-)$		
529	w, sh	$\nu_1 + \nu_4(\text{AlCl}_4^-)$		
563	w	?	580 ^d	Variable
658	vs	$\nu_3(\text{F}_2)(\text{PCl}_4^+)$	640	vs
707	vw	$\nu_1 + \nu_4(\text{PCl}_4^+)$	693	w
839	w	$\nu_3 + \nu_2(\text{PCl}_4^+)$		
970	vw	$2\nu_3(\text{AlCl}_4^-)$		
1111	vw	$\nu_3 + \nu_1(\text{PCl}_4^+)$		
1223	w	$2\nu_3(\text{PCl}_4^+)$		
1308	vw	?	1308	w

^a s, strong; vs, very strong; m, medium; w, weak, etc. ^b If there is no indication otherwise, the authors agree with the assignments of Carlson.²⁷ ^c $\nu_3(\text{F}_2)(\text{FeCl}_4)$. ^d $\nu_4(\text{E})(\text{POCl}_3)$; see ref 29.

of a simple crystal field model in which covalency was introduced by the use of parameters as determined by a molecular orbital calculation. The calculated frequencies of Table VI were obtained from the electrostatic matrices of Tanabe and Sugano.³⁰ The values of the crystal field parameter Dq and the Racah parameter B were taken from the recent molecular orbital calculations by Fenske and Radtke³¹ on the FeCl_4^- ion, while the Racah parameter C was varied in order to fit the spectrum. The results shown in Table VI are for a C/B ratio of 3.00 ($B = 625\text{ cm}^{-1}$, $C = 1875\text{ cm}^{-1}$). The assignments given have some favorable qualitative characteristics: (1) The strongest bands in the spectra are assigned to sextet-quartet transitions which are orbitally allowed in the point group $T_d(\text{A}_1 \rightarrow \text{T}_2)$.

(30) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

(31) R. F. Fenske and D. R. Radtke, *Inorg. Chem.*, **7**, 479 (1968).

TABLE VI
FREQUENCIES AND ASSIGNMENTS OF THE
SPECTRUM OF THE FeCl_4^- ION

ϵ , $\text{mol}^{-1} \text{l. cm}^{-1}$	ν , cm^{-1}		Assignment
	Exptl	Calcd ^a	
1.3	13,600	11,716	${}^6\text{A}_1 \rightarrow {}^4\text{T}_1(\text{a})$
1.2	14,400	14,486	${}^6\text{A}_1 \rightarrow {}^4\text{T}_2(\text{a})$
	15,650 ^b	14,805	${}^6\text{A}_1 \rightarrow {}^2\text{T}_2(\text{a})$
	16,000	15,625	${}^6\text{A}_1 \rightarrow {}^4\text{E}(\text{a})$
1.0	16,350	15,626	${}^6\text{A}_1 \rightarrow {}^4\text{A}_2$
	17,800 ^b	18,500	${}^6\text{A}_1 \rightarrow {}^2\text{A}_2(\text{a})$
1.8	18,650	18,738	${}^6\text{A}_1 \rightarrow {}^4\text{T}_2(\text{b})$
	19,500	19,194	${}^6\text{A}_1 \rightarrow {}^2\text{T}_1(\text{a})$
			$\rightarrow {}^4\text{E}(\text{b})$
			${}^6\text{A}_1 \rightarrow {}^2\text{E}(\text{a})$
			$\rightarrow {}^4\text{T}_1(\text{b})$
	21,750	20,000	$\rightarrow {}^2\text{T}_2(\text{b})$
			$\rightarrow {}^2\text{A}_1(\text{a})$
	20,386		
	20,878		
	21,467		
	21,800		

^a $Dq = -508 \text{ cm}^{-1}$; $B = 625 \text{ cm}^{-1}$; $C/B = 3.00$. ^b Taken from the 20°K spectrum of $(\text{PyH})_3\text{Fe}_2\text{Cl}_6$.⁸

(2) The bands observed only at low temperatures (20°K) are assigned to sextet-doublet transitions.

(3) Since the ${}^4\text{A}_2$ and ${}^4\text{E}$ states are degenerate only in the crystal field model, the assigned splitting of 350 cm^{-1} is not unreasonable.

For a more complete discussion of the possible effects of covalency, lower than cubic potential fields, spin-orbit coupling, and alternative assignments of the transitions in the FeCl_4^- anion, the recent article by Balt¹⁰ should be consulted.

Three common approximations which have been applied to correct bond lengths for the effects of anisotropic thermal motion are the rigid-body approximation of Cruickshank³² and the riding and independent motion of Busing and Levy.³³ The results of these calculations are compared in Table VII. The riding model and the rigid-body analysis predict almost the same values for the thermally corrected bonded distances. Comparatively speaking the independent motion model predicts larger corrections to the bonded distances. In view of the above calculations, it is felt that the most probable limits for the bonded distances

(32) D. W. J. Cruickshank, *Acta Cryst.*, **9**, 754 (1956).

(33) W. R. Busing and H. A. Levy, *ibid.*, **17**, 142 (1964).

TABLE VII
COMPARISON OF BOND LENGTHS
CORRECTED FOR THERMAL MOTION

Bond	Model applied			
	Uncorrected	Riding	Independent	Rigid body
Fe-Cl(1)	2.1819 (10)	2.2077 (11)	2.2453 (11)	2.201
Fe-Cl(2)	2.1873 (15)	2.2125 (16)	2.2466 (15)	2.207
Fe-Cl(3)	2.1869 (14)	2.2015 (14)	2.2424 (14)	2.200
P-Cl(4)	1.9123 (12)	1.9511 (12)	1.9992 (12)	1.941
P-Cl(5)	1.9024 (13)	1.9421 (13)	1.9922 (13)	1.929

are given by the riding motion model and the rigid-body analysis. The relatively large corrections to the bond distances (0.02–0.04 Å) emphasize again that one must be cautious in making anything but qualitative arguments based on thermally uncorrected bond distances. The standard deviations quoted for the uncorrected bond lengths ($\sim 0.001 \text{ Å}$) represent the internal consistency of the data and not necessarily the accuracy of the distances between nuclear centers.

The symmetry of the PCl_4^+ ion is more nearly tetrahedral in $[\text{PCl}_4][\text{FeCl}_4]$ than in PCl_5 as evidenced by the independent angles of 108.38, 108.30, 109.50, and 110.58° in $[\text{PCl}_4][\text{FeCl}_4]$ as compared to 111 and 119° in PCl_5 . The uncorrected phosphorus-chlorine bonded distances in $[\text{PCl}_4][\text{FeCl}_4]$ are substantially shorter than those in PCl_5 (1.91 and 1.90 vs. $\sim 1.97 \text{ Å}$). The shortening of the distances is probably due to two sources: (1) a higher degree of thermal motion and/or (2) a manifestation of more accurate positional parameters as determined by present day data collection and refinement techniques. The FeCl_4^- ion is also nearly tetrahedral. The bonded distances are very close to being within three standard deviations of each other for both the uncorrected and the thermally corrected data, and only one bond angle differs by more than about 1° from the tetrahedral angle of 109.50° .

The crystal packing is dominated by parallel linear arrays of PCl_4^+ and FeCl_4^- tetrahedra along [100]. The closest contact between nonbonded chlorines is 3.51 Å. The PCl_4^+ and FeCl_4^- ions are isolated from each other as evidenced by the Fe-P distance of 5.03 Å and the closest Fe-Cl (PCl_4^+) distance of 4.41 Å.