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Bridge Addition Compounds. IV. The Addition of Group IV Halides to Dicyanobis(1,10-phenanthroline)iron(II)

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Eleven new addition compounds have been formed between dicyano iron(II) complexes and Si, Ge, and Sn fluorides and chlorides. Three general types of adducts were found, with nominal acid to base ratios of 1:1, 2:1, and 3:1. The 1:1 complexes appear to be cyclic dimers, since molecular weight data for $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{SiF}_4$ and infrared data indicate this structure. The 2:1 complexes are monomeric in coordinating solvents and dimeric in noncoordinating solvents as indicated by molecular weight data for $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 2\text{GeF}_4$. An analysis of the equilibria between GeF_4 and $[\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 2\text{GeF}_4]_2$ in methylene chloride solution demonstrates the presence of two unusual adducts, $[\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 2.5\text{GeF}_4]_2$ and $[\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 3\text{GeF}_4]_2$. It is postulated that the fifth and sixth germanium tetrafluoride molecules are bound into these complexes exclusively by fluorine bridges.

Introduction

Previous work has demonstrated the basicity of transition metal coordinated cyanide and thiocyanate ligands toward boron-containing Lewis acids.¹ These compounds involve the formation of ligand-bridged adducts (e.g., $\text{Fe}-\text{C}\equiv\text{NBF}_3$) in which the Lewis acid can influence the electronic structure of the complex. For example, it was found that oxidation potentials and charge-transfer spectra parallel the acidity of the Lewis acid for a series of cyanide-bridged adducts, $\text{Fe}(\text{phen})_2(\text{CNBX}_3)_2$; $\text{X} = \text{F}, \text{Cl}, \text{Br}$.² This result was surprising, since the acidity (as measured by heat or free energy of adduct formation) and the electronic structure of the final adduct should follow different trends. The order of acidity has been explained in terms of the energy necessary to distort the initially planar acid to a pyramidal configuration required for adduct formation. This reorganization energy decreases upon going from BF_3 to BBr_3 .^{3,4} However, the electronic properties of the adduct should reflect the acceptor strength of the reorganized acid which from electronegativity arguments should fall in the order $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$. It is possible to rationalize the observed opposite order by invoking partial reorganization of the BX_3 groups. According to this argument the degree of reorganization would increase in the series $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$ which could lead to a similar order for the electron-pair affinities.

A study of the spectral shifts for group IV halide adducts of $\text{Fe}(\text{phen})_2(\text{CN})_2$ is relevant to this problem because reorganization energy appears to be less influential on the acidities of these molecules with the result that the order of acidity is the reverse of group III; that is, fluorides are more acidic than chlorides.⁵

We realized at the outset that the structures of

group IV adducts might be complex because both the acid MX_4 and the base $\text{Fe}(\text{phen})_2(\text{CN})_2$ are potentially difunctional. These systems conceivably could yield a variety of products ranging from cyclic adducts to high polymers,⁶ and a study of the molecular formulas of these adducts soon became a primary objective of this research.

The stoichiometry of formation has been determined for a large number of group IV halide adducts.⁵ However, very few quantitative equilibrium and molecular weight measurements have been performed. In the present work we were able to obtain such data, which indicate some unusual aggregates which are held together presumably by fluorine bridges.

Experimental Section

General Procedures.—Volatile Lewis acids, SiF_4 , GeF_4 , SiCl_4 , GeCl_4 , and SnCl_4 , were manipulated in a preparative high vacuum system. Kel F 90 was used as a stopcock lubricant. The tensimetric titrations, which involve prolonged exposure of the apparatus to solvent vapors, were carried out in a grease-free system which employed O-ring joints and a needle valve stopcock manufactured by Fischer and Porter Co. Stoichiometry of adduct formation was generally checked by several independent methods: tensimetric titration, net acid absorbed, and weight gain. The use of several criteria for the stoichiometry was prompted by a preliminary study in which $\text{Fe}(\text{phen})_2(\text{CN})_2$ and BF_3 in the presence of *s*-tetrachloroethane led to a complicated reaction with this solvent. Infrared spectra were determined on a prism-grating Beckman IR 9, and visible spectra were obtained on a Cary Model 14. The samples for spectral work were prepared as mineral oil or Fluorolube mulls in a nitrogen-filled glove bag. In separate experiments good agreement was found between visible reflectance minima for samples of the adduct (determined with a Cary diffuse reflectance integrating sphere attachment) and absorption maxima determined on Nujol mulls and methylene chloride solutions.

$\text{SiF}_4-\text{Fe}(\text{phen})_2(\text{CN})_2$.—Silicon tetrafluoride (Matheson) was purified by fractionation through a trap maintained at -126° into one at -196° . The vapor pressure, 124.7 mm at -111.6° , and infrared spectrum agreed with the literature.^{7,8} $\text{Fe}(\text{phen})_2(\text{CN})_2$ was prepared according to Schilt's recipe.⁹ The crude

(1) (a) D. F. Shriver, *J. Am. Chem. Soc.*, **84**, 4610 (1962); (b) D. F. Shriver, *ibid.*, **85**, 1405 (1963); (c) D. F. Shriver, A. Luntz, and J. J. Rupp, Proceedings of the Eighth International Conference on Coordination Chemistry, 1964, p 320.

(2) D. F. Shriver and J. Posner, *J. Am. Chem. Soc.*, **88**, 1672 (1966).

(3) H. C. Brown and R. R. Holmes, *ibid.*, **78**, 2173 (1956); also, A. W. Laubengayer and D. S. Sears, *ibid.*, **67**, 164 (1945).

(4) F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959).

(5) I. R. Beattie, *Quart. Rev.* (London), **17**, 382 (1963).

(6) Polymer formation has been observed for dinitrile adducts of group IV halides: M. Kubota and S. R. Schulze, *Inorg. Chem.*, **3**, 852 (1964).

(7) O. Ruff and E. Ascher, *Z. Anorg. Allgem. Chem.*, **196**, 413 (1931).

(8) E. Jones, J. Kirby-Smith, P. Woltz, and A. Nielson, *J. Chem. Phys.*, **19**, 242 (1951).

(9) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

material was washed with warm benzene to remove excess 1,10-phenanthroline and then was recrystallized from sulfuric acid.

A 0.724-mmole sample of $\text{Fe}(\text{phen})_2(\text{CN})_2$ was dehydrated under high vacuum, and 2 ml of methylene chloride was introduced by trap to trap distillation. The methylene chloride had been dehydrated over calcium hydride; its vapor pressure was 144.05 mm at 0° (lit.¹⁰ 144.0). A break in the pressure *vs.* composition curve was found at 1.0 SiF_4 per $\text{Fe}(\text{phen})_2(\text{CN})_2$ when the titration was conducted at -45.2° or at -22.9° .¹¹ Excess SiF_4 was removed under high vacuum and *PVT* measurement of the unreacted acid indicated a mole ratio of 1.02 while 1.01 was found by weight gain of the solid. The cyanide stretch frequency and also the visible charge-transfer spectrum displayed the characteristic shifts to higher energy.¹ The X-ray powder pattern of the compound (Table I) was distinct from the pattern of the parent iron complex. $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot x\text{SiF}_4$ is a red-brown solid which is only slightly soluble in methylene chloride and is decomposed by atmospheric moisture.

TABLE I
X-RAY POWDER DIFFRACTION DATA

Fe(phen) ₂ (CN) ₂ · xMX ₄							
Fe(phen) ₂ (CN) ₂		x = 1, MX ₄ = SiF ₄		x = 1, MX ₄ = GeF ₄		x = 2, MX ₄ = GeF ₄	
d, Å	Intensity	d, Å	Intensity	d, Å	Intensity	d, Å	Intensity
13.69	vw	11.95	vw	11.95	w	11.24	vw
9.82	vw	8.66	m	8.63	w	9.54	vw
8.36	m	8.36	m				
7.62	vs						
7.07	vs	6.92	w	7.03	w	7.26	s
6.13	m, br	6.11	vs	6.11	vs	6.24	vs
4.84	vs			5.52	w		
3.90	s	5.24	w	5.24	w	5.25	vw
3.72	s	4.89	vw	4.89	vw	4.81	w
3.32	w	4.54	m	4.54	ms	4.49	w
2.94	vw	4.14	s	4.14	s	4.14	m
2.74	vvw	3.92	vw	3.87	vw	3.83	w
2.56	vw	3.48	ms	3.48	ms	3.50	w
2.08	vvw	2.73	w	2.73	m	2.94	vw
		2.49	vw			2.75	w
		2.35	w				
		2.26	w	2.26	w		

Under more favorable conditions, higher SiF_4 adducts were formed. When a tenfold excess of SiF_4 was added to a $\text{Fe}(\text{phen})_2(\text{CN})_2$ sample in CH_2Cl_2 and the temperature maintained at -78° , a yellow adduct was formed, but above -30° the color changed to red-brown, reminiscent of the 1:1 complex. Upon recooling the sample to -78° , the bright yellow color returned; removal of the solvent and unreacted acid at -45° left a yellow solid which upon prolonged pumping under high vacuum yielded a brown 2:1 adduct (2.00 by net acid complexed and 1.97 by weight gain). In the absence of solvent this 2:1 adduct was stable at room temperature. When a SiF_4 atmosphere was placed over the brown 2:1 adduct, the solid turned yellow, even at room temperature and in the absence of solvent. When excess acid was removed from the solid at -78° a yellow 2.5:1 adduct was reproducibly obtained.

SiF_4 - $\text{Fe}(\text{phen})_2(\text{CN})_2$.—The low solubility of $\text{Fe}(\text{phen})_2(\text{CN})_2$ and its adducts in suitable solvents precluded molecular weight and equilibrium measurements and prompted the preparation of a more soluble "bathophenanthroline" analog. The dicyanobis(4,7-diphenyl-1,10-phenanthroline)iron(II) complex, $\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2$, was prepared by a procedure similar to that used for $\text{Fe}(\text{phen})_2(\text{CN})_2$; however, a different purification procedure was necessary. The complex and excess ligand were separated by adsorption chromatography on a neutral alumina

column. For this purpose Merck acid-washed alumina was made alkaline and then washed with water until a pH of 7 was attained. This material was dried at 90° . An acidic alumina column did not separate the components, while a basic column led to partial decomposition of the complex. The excess ligand was eluted with chloroform and finally the deep blue complex was eluted with ethyl alcohol. *Anal.* Calcd: Fe, 7.23; N, 10.88, mol wt, 772.7. Found: Fe, 7.06; N, 10.54; mol wt, 773 ± 7 (Rast method). The melting point in a sealed tube under a nitrogen atmosphere is 265° . In ethanol solution this complex had an absorption maximum at $582 \text{ m}\mu$ (ϵ 13,980).

In a previous report of this compound, Diehl and Buchanan observed two absorption maxima of nearly equal intensity at 530 and 610 $\text{m}\mu$ for chloroform solutions.¹² In the same solvent, our material exhibits a maximum at 618 $\text{m}\mu$ (ϵ 18,300) and a shoulder at *ca.* 563 $\text{m}\mu$ (ϵ 13,340). This spectrum is similar to that of $\text{Fe}(\text{phen})_2(\text{CN})_2$, which has a maximum at 598 $\text{m}\mu$ and a shoulder at 546 $\text{m}\mu$. We believe that Diehl and Buchanan's preparation was contaminated with a small amount of $\text{Fe}(\text{phen}\phi_2)_2^{2-}$, which has an absorption maximum at 528 $\text{m}\mu$ and which was present in our crude material but was retained by the alumina chromatographic column.

A tensimetric titration in methylene chloride showed 1.0 SiF_4 absorbed per $\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2$ at -22.9° and at -45.2° (Figure 1). Removal of volatiles under high vacuum followed by trap to trap distillation from the solvent and *PVT* measurement of unconsumed SiF_4 indicated a mole ratio of 1.00 and weight gain indicated 1.01. Molecular weight determination on the complex in chloroform solution by vapor pressure osmometry¹³ showed 1.97 formula weights per molecule, while a molecular weight determination by the Rast method indicated 1.99 for the degree of aggregation. In a sealed tube filled with nitrogen the red-brown complex melted and decomposed to a blue material at 273 – 277° .

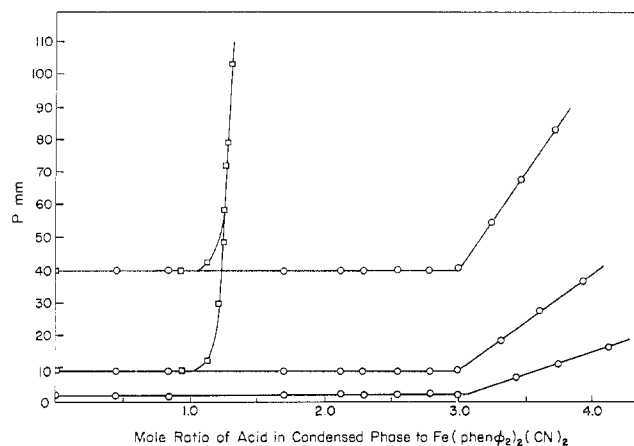


Figure 1.—Tensimetric titration of $\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2$ with SiF_4 , —□—, and GeF_4 , —○—. Bottom curve -63.5° , middle curves -45.2° , upper curves -22.9° .

$\text{Fe}(\text{phen})_2(\text{CN})_2$ - GeF_4 .—Germanium tetrafluoride was prepared by the thermal decomposition of barium hexafluorogermanate¹⁴ and was purified by condensation at -111.6° while more volatile impurities were pumped away. Purity was checked by an infrared spectrum which showed the absence of SiF_4 and agreed with a published spectrum;¹⁵ also, the vapor pressure, 57.4 mm at -63.5° , remained constant upon removal of GeF_4 . This vapor pressure is significantly lower than reported by either Dennis and Laubengayer (83.1 mm interpolated to -63.5°)¹⁴ or

(12) H. Diehl and E. Buchanan, Jr., *Talanta*, **1**, 76 (1958).

(13) Mechrolab, Model 302, Mountain View, Calif.

(14) L. M. Dennis and A. W. Laubengayer, *Z. Physik. Chem. (Leipzig)*, **130**, 520 (1927).

(15) A. Caunt, L. Short, and L. Woodward, *Trans. Faraday Soc.*, **48**, 873 (1952).

(10) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

(11) When simple mole ratios are quoted they represent moles of acid per mole of base. Most of the reactions were conducted on the scale described here.

Fisher and Weidemann (70.7 mm interpolated to -63.5°).¹⁶ These vapor pressures are probably high due to SiF_4 contamination which was not detected by earlier workers who did not have the use of infrared spectrometers. As a further check on the purity of our GeF_4 , the molecular weight was determined by vapor density: obsd 148.5, calcd 148.6. The GeF_4 was easily handled in the Pyrex vacuum system without sign of decomposition; however, prolonged contact (ca. 2 weeks) with Pyrex led to etching of the glass and the appearance of strong SiF_4 absorptions in its infrared spectrum.

Surprisingly, tensimetric titration of $\text{Fe}(\text{phen})_2(\text{CN})_2$ with GeF_4 indicated 3.0 moles of acid was absorbed per mole of base at -45.2° and at -22.9° . The dissociation pressure of this adduct was quite low at -45.2° which allowed removal of solvent and excess acid at this temperature. Since GeF_4 and CH_2Cl_2 could not be separated by trap to trap distillation, excess GeF_4 was determined by the weight of the well-known pyridine adduct,¹⁷ $\text{GeF}_4 \cdot 2\text{py}$, which showed a net uptake of 2.99 moles of GeF_4 per mole of cyanide complex. At temperatures above -30° the dissociation pressure of $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 3\text{GeF}_4$ was noticeable and pressure measurements were performed over the range -22.9 to $+45.0^\circ$ (Table II). To check the constancy of the equilibrium pressures with changes in gross composition of the solid, about half of the GeF_4 was removed at 0° without a significant change in GeF_4 pressure. Prolonged evacuation of the solid produced a stable 2:1 adduct (2.05 from excess GeF_4 determination and 2.01 from weight gain of the solid). Both the 2:1 and the 3:1 adducts are orange.

TABLE II

DISSOCIATION PRESSURES OF $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 3.0\text{GeF}_4$

$T, ^\circ\text{C}$	P, mm^a	$T, ^\circ\text{C}$	P, mm^a
-45.2	0.00	33.15	74.75
-22.9	2.80	37.00	81.22
0.00	11.99	40.00	90.57
19.40	33.89	45.00	113.76

^a These pressures have been corrected for the density of mercury at room temperature and for the local value of the acceleration due to gravity.

A 1:1 GeF_4 analog of the SiF_4 adduct was prepared by the distillation of GeF_4 onto an equimolar amount of $\text{Fe}(\text{phen})_2(\text{CN})_2$ in methylene chloride, followed by constant stirring for several hours at room temperature. All of the GeF_4 was absorbed to yield a brown-red adduct. This adduct did not display an absorption band at $600 \text{ m}\mu$ which would have been characteristic of uncomplexed $\text{Fe}(\text{phen})_2(\text{CN})_2$, and terminal CN stretching frequencies (ca. 2080 cm^{-1}) were absent. Spectral data are summarized in Figure 2 and Table III. An X-ray powder pattern (Table I) of the 1:1 GeF_4 adduct indicates isomorphism with the 1:1 SiF_4 compound. When formation of a 1:1 adduct was attempted at -22.9° , a homogeneous product was not realized.

$\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2 \cdot \text{GeF}_4$.—Tensimetric titration of $\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2$ in methylene chloride indicated 3.0 moles of acid was absorbed per mole of base at -45.2 , -22.9 , and 0.0° (Figure 1). The adduct formed was completely soluble in methylene chloride. Fast removal of the solvent and excess acid at -45.2° left a yellow 3:1 adduct (3.01 from excess GeF_4 determination and from weight gain of the solid) which was stable to further pumping at temperatures of at least 50° . Tensimetric titration of $\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2$ in toluene indicated 2.0 moles of acid absorbed per mole of base at -45.2 , -22.9 , and 0.0° . This orange adduct was insoluble in the toluene. Addition of exactly 2.00 moles of GeF_4 per mole of $\text{Fe}(\text{phen})_2(\text{CN})_2$ in methylene chloride gave an orange 2:1 adduct which does not appear to lose GeF_4 in solution or in the solid state. This material is identical with the orange 2:1 adduct obtained from the reaction in toluene.

(16) W. Fisher and W. Weidemann, *Z. Anorg. Allgem. Chem.*, **213**, 106 (1933).

(17) E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).

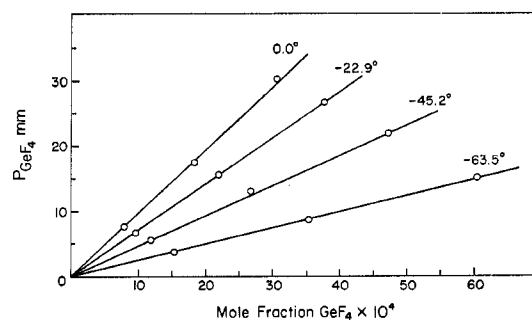
Figure 2.—Solubility of GeF_4 in methylene chloride.

TABLE III

C≡N STRETCHING FREQUENCIES AND VISIBLE SPECTRA

Compound	$\nu(\text{CN}), \text{cm}^{-1}$	Visible $\lambda, \text{m}\mu$
$\text{Fe}(\text{phen})_2(\text{CN})_2$	2067, 2081	620, ca. 545 sh
$\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{SiF}_4$	2162	525, ca. 477 sh
$\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{GeF}_4$	2148	501, ca. 458 sh
$\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{SnF}_4$	2132	488, ca. 444 sh
$\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2$	2084	647, ca. 572 sh
$\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2 \cdot \text{SiF}_4$	2090	613
$\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{SiF}_4$	2138, 2155	486, ca. 444 sh
$\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{GeF}_4$	2134	459
$\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 2\text{SnF}_4$	2114	497
$\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2 \cdot 2\text{GeF}_4$	2130	496, ca. 456 sh
$\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2 \cdot 3\text{GeF}_4$	2129	481, ca. 452 sh
$\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 0.75\text{SiCl}_4$	2131	505
$\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{GeCl}_4$	2095, 2104	517, ca. 477 sh
$\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{SnCl}_4$	2104	488, ca. 450 sh

Molecular weight measurements on the 2:1 adduct using the Rast method indicated a molecular weight of 1066 ± 23 . Vapor pressure depression of a 2.48 mole % methylene chloride solution at 25.3° gave a molecular weight of 2224. A 1.48 mole % solution gave molecular weight values of 2191 at 25.3° and 2199 at 0.0° . The calculated formula weight for $\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2 \cdot \text{GeF}_4$ is 1070, giving a state of aggregation of 0.996 in camphor and 2.08 to 2.05 in methylene chloride.

Molecular weight data for the $\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2 \cdot 3\text{GeF}_4$ complex could not be obtained because a finite dissociation pressure of germanium tetrafluoride existed over the solution. At the composition 2.0:1, complete solution was attained in methylene chloride at 20° and down to -15° depending on the concentration of the particular solution. Between the compositions of 2.0:1 and 2.5:1, the temperature above which complete solubility was observed remained approximately constant for a particular solution. At the composition 2.5:1 a great increase in solubility was noted.

$\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{SnF}_4$.—One ml of reagent grade methanol which had been conditioned by exposure to SnF_4 was distilled onto an equimolar mixture of SnF_4 and $\text{Fe}(\text{phen})_2(\text{CN})_2$ (0.606 mmole of each). After 24 hr of stirring a homogeneous product resulted, and the methanol was removed under vacuum. The weight of the red solid product was the same as the weight of the reactants.

Under similar conditions, twice the equivalent amount of SnF_4 (0.485 mmole) was added to the $\text{Fe}(\text{phen})_2(\text{CN})_2$ (0.242 mmole). The mixture was continuously stirred for 24 hr, and a homogeneous product resulted. Removal of the solvent under vacuum left a yellow product which had the same weight as that of the reactants.

X-Ray powder patterns of the SnF_4 adducts could not be obtained. The exposures showed only amorphous scattering.

$\text{SiCl}_4 \cdot \text{Fe}(\text{phen})_2(\text{CN})_2$.—Purified SiCl_4 exhibited a vapor pressure of 75.4 mm at 0° (lit.¹⁸ 79.0 mm). The low volatility of the SiCl_4 prevented tensimetric titrations in methylene chloride.

(18) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, New York, N. Y., 1948, p 147.

Since no convenient means of separating SiCl_4 and CH_2Cl_2 was found, stoichiometry of adduct formation was determined solely by weight gain of the solid. Reactions were run with stoichiometric 1:1 ratios and with excess SiCl_4 . After reaction, the volatiles were removed at temperatures varying from that of the room down to -45.2° . In some experiments pure SiCl_4 was placed on the solid after reaction and solvent removal. From all variations attempted, the same yellow solid having the SiCl_4 : $\text{Fe}(\text{phen})_2(\text{CN})_2$ ratio of 0.75:1 was isolated. No uncomplexed cyanide or decomposition of the reactants or solvent was observed in infrared and visible spectra. In the experiments in which equimolar amounts of SiCl_4 and $\text{Fe}(\text{phen})_2(\text{CN})_2$ were present, the gas-phase infrared spectrum of the volatile removed after reaction contained an identifiable SiCl_4 absorption.

GeCl_4 - $\text{Fe}(\text{phen})_2(\text{CN})_2$.—Germanium tetrachloride was purified by vacuum line distillation into a trap held at -78° , while the principal impurity, HCl , was pumped away (vapor pressure 24.1 mm at 0° , lit.^{19a} 25 mm). Because of the relatively low vapor pressure of GeCl_4 , tensimetric titration was impractical. Reaction of GeCl_4 with $\text{Fe}(\text{phen})_2(\text{CN})_2$ in 1,2-dichloroethane for 4 days at room temperature followed by removal of the solvent and excess GeCl_4 under high vacuum for several hours led to a weight gain corresponding to 1.05 GeCl_4 per $\text{Fe}(\text{phen})_2(\text{CN})_2$. The orange-red solid did not change weight or color after 12 hr exposure to high vacuum. The $\text{C}\equiv\text{N}$ stretch frequencies (Table III) were increased upon formation of the GeCl_4 complex.

SnCl_4 - $\text{Fe}(\text{phen})_2(\text{CN})_2$.—Reagent grade SnCl_4 was distilled into the vacuum line and HCl was removed under vacuum at -78° (vapor pressure 5.25 mm at 0° , lit.^{19b} 5.2). Tin tetrachloride reacts slowly with mercury and has an inconveniently low vapor pressure, so a tensimetric titration was not attempted. The reactions were performed in a grease and mercury free O-ring system, and the SnCl_4 was measured by weight change of the reservoir from which it was distilled. This reservoir was equipped with a needle-valve stopcock and O-joint. Equimolar quantities of SnCl_4 (0.249 mmole) and $\text{Fe}(\text{phen})_2(\text{CN})_2$ (0.246 mmole) were stirred in contact with methylene chloride for 60 hr. After this period of time, the color of the product was a homogeneous orange-red. The weight of the solid, after removal of the solvent under high vacuum, indicated 1.00 SnCl_4 was retained per $\text{Fe}(\text{phen})_2(\text{CN})_2$.

Addition of more than 2 moles of SnCl_4 per mole of iron complex followed by prolonged stirring and removal of volatiles did not give reproducible results. The maximum amount of SnCl_4 absorbed per $\text{Fe}(\text{phen})_2(\text{CN})_2$ was 1.6 and internal checks on the experiment were poor. The source of these complications is unknown.

Equilibrium Calculations.—These calculations were undertaken to determine the molecular formula of the 3:1 adduct, $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 3\text{GeF}_4$. The most conveniently measured variable was the total pressure of gas ($\text{GeF}_4(\text{g})$ plus $\text{CH}_2\text{Cl}_2(\text{g})$) above the equilibrated solution. To obtain descriptive equilibrium constants the concentration of free GeF_4 in solution was required and this was determined from Henry's law after a Raoult's law correction was applied for the solvent vapor pressure.

As illustrated in Figure 2 the solubility of GeF_4 in methylene chloride is accurately represented by Henry's law. The constants obtained at several temperatures were: 2.50×10^3 at -63.5° ; 4.77×10^3 at -45.2° ; 7.14×10^3 at -22.9° ; 9.58×10^3 mm (m.f.)⁻¹ at 0.00° . After these values were determined, a value for the Henry's law constant at 20.00° was required and this was found from an extrapolation of the linear plot of \ln (m.f. GeF_4) vs. T^{-1} at constant GeF_4 partial pressure. The value obtained is 1.30×10^4 mm (m.f.)⁻¹.

It was known from the vapor pressure depression of CH_2Cl_2 by $\text{Fe}_2(\text{phen})_4(\text{CN})_4 \cdot 2\text{GeF}_4$ that the solution obeys Raoult's law, and it was assumed that solutions of higher complexes would behave similarly. The least involved cases are 2 and 3 (see

Discussion). For these, the extent of reaction does not influence the total concentration of iron-containing species, and therefore it does not affect the vapor pressure of the solvent. The partial pressure of germanium tetrafluoride was calculated from the total pressure by Raoult's law correction of the methylene chloride vapor pressure for all dissolved species (iron complexes plus dissolved GeF_4). This was accomplished in an iterative manner (see Figure 3). At this point the concentration of GeF_4 was calculated through Henry's law and the equilibrium constant(s) for either process 2 or 3 was found by conventional means. For process 3 a graphical method²⁰ provided a convenient source of initial equilibrium constants which were then refined by successive approximations.

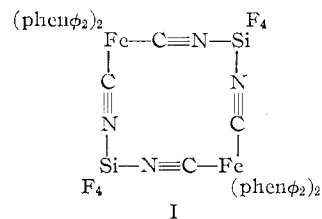
Since equilibrium 1 involves a change in the state of aggregation of the complex, the extent of reaction influences the vapor pressure of the solvent. Therefore, the equilibrium calculations had to be included in each cycle of computation of GeF_4 partial pressure.

In a typical equilibrium experiment, 16.896 mmoles of CH_2Cl_2 and 0.1294 mmole of $\text{Fe}(\text{phen})_2(\text{CN})_2$ were used. The equilibrium data in the 2:1 to 3:1 germanium to iron composition range were obtained from several incremental additions within a 16-hr time period. Prolonged experiments with many data points were avoided because a decomposition occurred after 36 hr. This decomposition led to the formation of a gray solid, etching of the inner walls of the Pyrex system, and formation of SiF_4 . However, within 24 hr no sign of SiF_4 could be found in the infrared spectra of the gas above the solution.

Discussion

From the data in the previous section it is clear that the silicon tetrahalide complexes are less stable than their germanium analogs. Also, the cyanide complex has a higher affinity for SiF_4 than SiCl_4 and GeF_4 than GeCl_4 . Similar trends are frequently observed for group IV acids.⁵

1:1 Adducts.—Previous work on cyanide complexes has demonstrated that upon bridge formation the $\text{C}\equiv\text{N}^-$ stretching frequency increases significantly.^{1,21} This observation has a direct bearing on the 1:1 adducts since these compounds display an increase in $\text{C}\equiv\text{N}^-$ stretching frequency and give no indication of remaining terminal $\text{C}\equiv\text{N}^-$ groups. Furthermore, molecular weight measurements on $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{SiF}_4$ in chloroform and camphor indicate this 1:1 adduct is dimeric. Therefore, we propose the following cyclic structure.



Because of their low solubility, molecular weight measurements were not possible with the 1:1 adducts of $\text{Fe}(\text{phen})_2(\text{CN})_2$. A common structure for the adducts is suggested by the observation that the 1:1 SiF_4 and GeF_4 adducts of $\text{Fe}(\text{phen})_2(\text{CN})_2$ are isomorphous (Table I) and presumably isostructural. As discussed

(20) F. C. J. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, pp 83-94.

(21) (a) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961); (b) D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, **4**, 725 (1965); (c) T. L. Brown and M. Kubota, *J. Am. Chem. Soc.*, **83**, 4175 (1961).

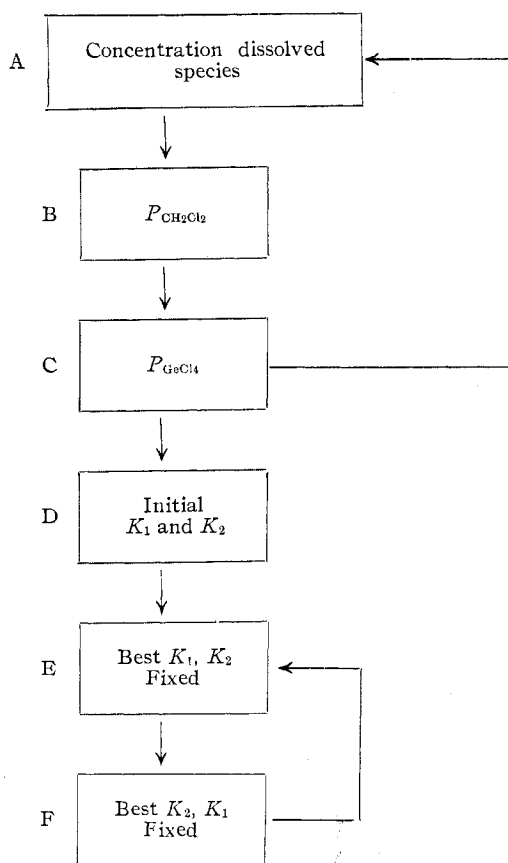


Figure 3.—Schematic representation of the calculation of equilibrium constants for eq 3. The concentration of dissolved species is initially calculated (A) from the quantity of iron complex, $\text{Fe}(\text{phen}\phi_2)_4(\text{CN})_4 \cdot 4\text{GeF}_4$, present. $P_{\text{CH}_2\text{Cl}_2}$ is calculated (B) using Raoult's law. P_{GeCl_4} is calculated (C) from the observed total pressure minus $P_{\text{CH}_2\text{Cl}_2}$. The pressure of GeF_4 calculated in step C is used to calculate dissolved GeF_4 which is included in second and subsequent calculations of step A. Steps A, B, and C are iterated until the partial pressures are constant. In step D, initial equilibrium constants are estimated graphically. Steps E and F involve a refinement of the equilibrium constants.

below, M-X vibrational frequencies are also consistent with the dimeric structure.

The two possible idealized local configurations for bi-coordinated MX_4 groups are *cis* and *trans*. The *cis* complex should have no degeneracies among its M-X stretching frequencies and four such absorptions are expected. However, the high symmetry of the *trans* complex leads to the expectation that there should be only one infrared-active M-X stretch absorption. From a study of model compounds, Hickie and Onyszchuk have concluded that these expectations are partially met.²² In particular, the *cis* complexes display three M-X stretch absorptions while the *trans* complexes appear to have only one such frequency. Our results for the 1:1 complexes, along with some pertinent frequencies of model compounds from ref 22, are presented in Table IV. The *cis* structure which is indicated by these data is required for a cyclic dimeric structure like I.

(22) (a) G. H. Hickie and M. Onyszchuk, paper presented at the Structural Inorganic Chemistry Symposium, Halifax, Nova Scotia, Sept 1965. We are indebted to Professor Onyszchuk for a preprint of this paper. (b) See also I. R. Beattie, et al., *J. Chem. Soc.*, 1514 (1963); 238 (1964).

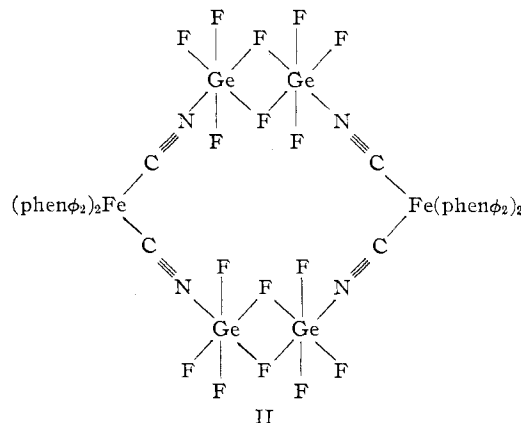
TABLE IV
M-X "STRETCH" FREQUENCIES

Complex ^a	Configuration	ν_{MX} , cm^{-1}
$\text{SiF}_4 \cdot 2\text{py}^b$	<i>trans</i>	795
$\text{GeF}_4 \cdot 2\text{py}$	<i>trans</i>	615 ^{b,c}
$\text{SiF}_4 \cdot \text{dipy}^b$	<i>cis</i>	795, 765, 742
$\text{GeF}_4 \cdot \text{dipy}^b$	<i>cis</i>	633, 619, 610
$\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{SiF}_4$		816 m, 808 m
$\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{GeF}_4$		642 s, 624 s, 599 ms
$\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot \text{SnF}_4$		590 sh, s, 478 s

^a py = pyridine; dipy = α, α' -dipyridine. ^b Ref 22a. ^c In our work the GeF stretch was observed at 619 cm^{-1} .

2:1 Adducts.—The infrared spectra of the 2:1 complexes showed all cyanide groups to be in bridging environments and the M-F stretching frequencies to be in the region expected for hexacoordinate group IV atoms. The molecular weight data of $\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2 \cdot 2\text{GeF}_4$ in methylene chloride indicate a dimeric structure which is presumably held together by means of fluorine bridges to give hexacoordinated group IV atoms. In camphor the molecular weight data indicate a monomer. Presumably, camphor functions as a coordinating solvent due to the presence of a carbonyl group which can displace fluorine bridges and occupy the sixth site on germanium.

A reasonable structure consistent with the data is II.



Another structure which was considered involves the coordination of two additional GeF_4 groups to terminal fluorines of structure I; however, contrary to the observed molecular weight in camphor, this compound should give three particles in a coordinating solvent. Structures involving GeF_6^{2-} ion formation were discounted because of the absence of a new band near 600 cm^{-1} .

The 2:1 SiF_4 adduct, $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 2\text{SiF}_4$, had a peculiar absorption at 930 cm^{-1} . Neither the 2:1 GeF_4 and SnF_4 nor the 1:1 SiF_4 adducts had an analogous infrared band. Schnell²³ found a similar absorption when examining the interaction of SiF_4 and $\text{N}(\text{CH}_3)_3$. The $\text{SiF}_4 \cdot \text{N}(\text{CH}_3)_3$ complex, which corresponds to the 2:1 complex of this work, had an infrared absorption at 940 cm^{-1} , while the $\text{SiF}_4 \cdot 2\text{N}(\text{CH}_3)_3$ did not. In both the present work and that of Schnell, an infrared absorption at $930\text{--}940 \text{ cm}^{-1}$ for SiF_4 adducts occurred only for complexes which conceivably could

(23) E. Schnell, *Monatsh. Chem.*, **93**, 1136 (1962).

have bridging fluorines, $\text{Fe}_2(\text{phen})_4(\text{CN})_4 \cdot 4\text{SiF}_4$ and $[\text{SiF}_4\text{N}(\text{CH}_3)_3]_2$. A possible explanation is that this absorption is due to bridged fluorines, although there is no precedent for an increase in frequency upon halide bridge formation.

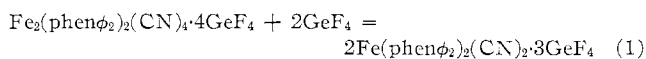
A fluorine-19 nuclear magnetic resonance experiment was attempted on a 2 mole % solution, the highest possible, of $\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2 \cdot 2\text{GeF}_4$ in methylene chloride but no resonance was observed, even though the sweep range was sufficiently broad, about 750 ppm on either side of the trifluoroacetic acid resonance, to have encompassed the resonance area of the 2:1 adduct. A 2 mole % solution of hexafluoro-2,2',3,3'-tetrachlorobutane gave a fairly strong signal. Evidently, all the fluorines in the adduct are not equivalent. If they were equivalent, a signal comparable to that of the fluorinated butane should have been observed. A structure such as that proposed for the 2:1 adduct (II) would have four types of fluorines and additional splitting is possible due to spin-spin interaction.

3:1 Adducts.—With monofunctional bases it is recognized that group IV halides sometimes add either 1 or 2 moles of base, thus there is precedent for all of the adducts in Table IV except for the 3:1 GeF_4 complex. There are no obvious sites for attachment of this third mole of GeF_4 . The adduct displays a high GeF_4 vapor pressure (Table II), and the derived values,²⁴ $\Delta S^\circ = 23.6 \pm 0.3 \text{ cal deg}^{-1} \text{ mole}^{-1}$, $\Delta H^\circ = 8.68 \pm 0.08 \text{ kcal mole}^{-1}$, for the process $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 3\text{GeF}_4(\text{s}) = \text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 2\text{GeF}_4(\text{s}) + \text{GeF}_4(\text{g})$ are close to the values $\Delta S^\circ_{298} = 26.7 \text{ cal deg}^{-1} \text{ mole}^{-1}$, $\Delta H^\circ = 7.9 \text{ kcal mole}^{-1}$ for the sublimation of GeF_4 .⁸ Also, a low-temperature infrared spectrum of $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 3\text{GeF}_4$ in a Hornig-type cell²⁵ failed to show any profound changes from $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 2\text{GeF}_4$. If it were not for the solution equilibrium data which are described below we would be inclined to conclude that this third GeF_4 is retained in the solid by van der Waals forces, to produce a solid solution. However, one argument against a solid solution phenomenon is the constancy of the vapor pressure for this compound at two different gross compositions between 2:1 and 3:1, which indicates $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 3\text{GeF}_4$ is a distinct phase.

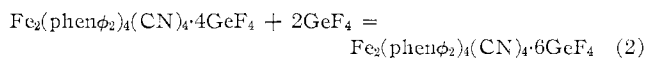
Convincing evidence that the 3:1 adduct is a true compound and not a lattice compound was obtained in the tensimetric titration of $\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2$ with GeF_4 (Figure 1). In this case no precipitate formed but the pressure-composition curve shows a clean break at 3:1 stoichiometry. Molecular weight data for $\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2 \cdot 3\text{GeF}_4$ could not be obtained, because it has a significant GeF_4 dissociation pressure and exists in equilibrium with lower complexes. In order to determine the nature of this adduct, the equilibria within the 2:1 to 3:1 stoichiometric region were studied. The equilibria which warranted consideration were limited by two previous observations. (1) Molecular

weight measurements had shown that the 2:1 complex is dimeric in methylene chloride solution. (2) Titration data at -22.9° and below indicated a 3:1 stoichiometry was the highest attained.

Equilibrium equations can be written for the 4:2 complex going to either a 3:1 monomer or 6:2 dimer.

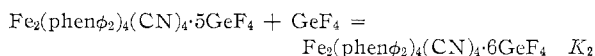
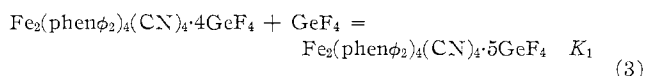


Equilibrium constants calculated for this equation were found to vary from 6.7×10^5 to 8×10^4 at 0.0° and from 3.0×10^4 to 1.3×10^4 at 20.0° as the Ge:Fe ratio increased from 2:1 to 3:1.



The equilibrium constants calculated for this equation also decreased with increasing Ge:Fe ratios: 1.5×10^9 to 8×10^6 at 0.0° and 2.1×10^7 to 1.5×10^6 at 20.0° .

By invoking a dimeric 5:2 intermediate a pair of equilibrium equations can be postulated



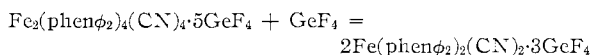
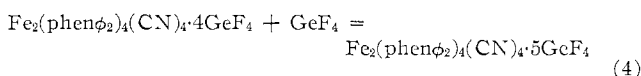
It may be seen in Table V that these equilibria did give constant calculated values for the equilibrium constants, K_1 and K_2 , with increasing Ge:Fe ratios.

TABLE V
VALUES OF EQUILIBRIUM CONSTANTS CALCULATED FOR EQUILIBRIUM PROCESSES 3^a

Ge/2Fe ^b	0.0°		20.0°		
	$K_1 \times 10^{-4}$	$K_2 \times 10^{-4}$	Ge/2Fe ^b	$K_1 \times 10^{-3}$	$K_2 \times 10^{-3}$
4.61	2.38	4.95	4.26	3.36	1.15
5.06	2.38	5.09	4.49	3.28	1.15
5.07	2.38	4.44	4.84	3.43	1.15
5.44	2.37	4.94	5.10	3.26	1.15
5.71	2.38	4.78	5.16	3.26	1.15
5.73	2.40	4.95	5.33	3.26	1.16
5.85	2.38	4.94	5.37	3.26	1.16
			5.49	3.26	1.13

^a Equilibria 1, 2, and 4 (see text) and 3 are homogeneous. A hypothetical mole fraction unity standard state is used for all species. ^b These ratios represent moles of GeF_4 bound in the complexes per 2 moles of the original $\text{Fe}(\text{phen}\phi_2)_2(\text{CN})_2$.

Another two-step equilibrium can be postulated



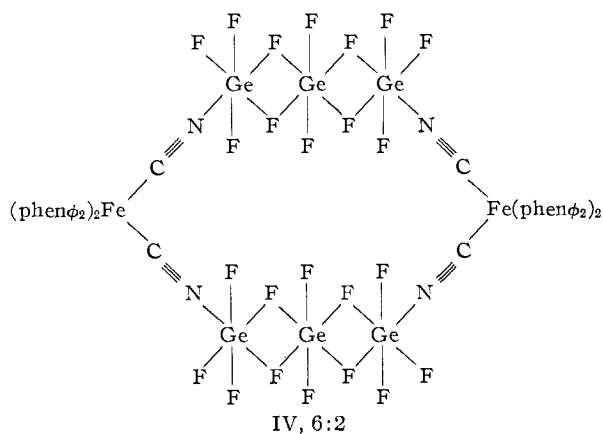
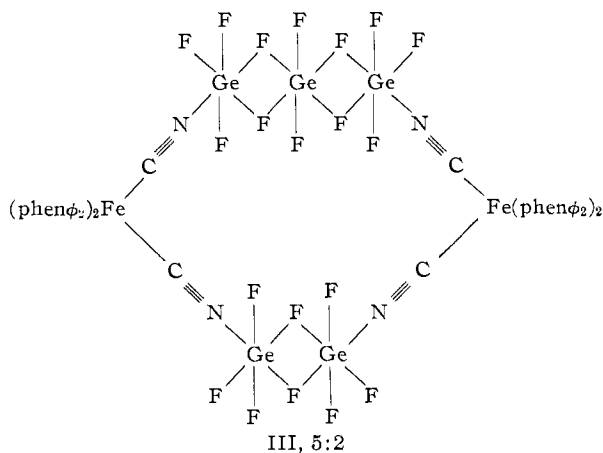
This may be viewed as eq 3 with an additional equilibrium involving the break-up of the 6:2 dimer to the 3:1 monomer. In view of the constancy of the equilibrium constants calculated for eq 3 this break-up does not occur to a significant extent.

The correct equilibrium equations (3) show the presence of two adducts, 5:2 and 6:2, and possible structures for these complexes are given below (III and

(24) The values of ΔH° and ΔS° were obtained by use of a least-squares program in which all the error was assumed to be in the pressure readings.

(25) E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 296 (1950).

IV).²⁶ These structures may be derived by successive insertion of GeF_4 into opposite corners of the proposed structure of the 4:2 compound (II).



Ionic structures appear to be excluded by the infrared data. For one of the possible ionic products, GeF_6^{2-} , Griffith and Irish²⁷ found that the Ge-F frequency at 600 cm^{-1} is unshifted by a variety of cations. In our work the 2:1 and 3:1 GeF_4 complexes exhibit Ge-F absorption at 645 to 680 cm^{-1} which are too high to attribute to GeF_6^{2-} . Also, if MF_6^{2-} were formed, a species of the type $-\text{N}-\text{MF}_3^+$ would probably be formed. For this substructure the group IV atom would be four-coordinated and two MF frequencies are expected. In the case of XSiF_3 the SiF bands would fall around 970 – 1000 cm^{-1} for the asymmetric stretch and 860 cm^{-1} for the symmetric stretch.²⁸ Aside from some phenanthroline absorptions, the 2:1 and 3:1 adducts did not display infrared bands in these regions.

The cyanide stretching frequency of the 3:1 complex, $\text{Fe}_2(\text{phen}\phi_2)_4(\text{CN})_4\cdot 6\text{GeF}_4$, was the same as that of the 2:1 complex. This normal CN stretch indicates that the third GeF_4 is not bound to the cyanide π system because a π adduct is expected to decrease greatly the cyanide stretching frequency. Furthermore, the small

(26) It should be recalled that qualitative solubility observations for the $\text{GeF}_4\text{-Fe}(\text{phen}\phi_2)_2(\text{CN})_2$ complex showed a sudden increase in solubility when 2.5 moles of GeF_4 was absorbed and that an unstable 2.5:1 adduct was the highest obtainable in the system $\text{SiF}_4\text{-Fe}(\text{phen})_2(\text{CN})_2$. Both of these results are explainable in terms of 5:2 adduct formation.

(27) J. E. Griffith and D. E. Irish, *Inorg. Chem.*, **3**, 1134 (1964).

(28) (a) H. Kriegsmann and K. H. Schowtka, *Z. Physik. Chem.* (Leipzig), **209**, 261 (1958); (b) C. Newman, S. R. Polo, and M. K. Wilson, *Spectrochim. Acta*, **15**, 793 (1959).

increase in frequency for the charge-transfer band of the 3:1 complex as compared to the 2:1 complex is expected for an interaction occurring inductively through the germanium attached to the nitrogen end of the cyanide.² Apparently, the 5:2 and 6:2 adducts represent a new type of compound in which the fifth and sixth germanium tetrafluoride molecules are retained in the complex solely by means of fluorine bridges. These compounds are believed to be the first of this type involving a group IV tetrahalide.²⁹

Unlike the next heavier group IV fluoride, SnF_4 , germanium tetrafluoride does not tend to self-associate. However, association through fluorine bridges does occur in the proposed structures. Apparently, the addition of a base to GeF_4 induces sufficient basicity in the remaining fluorines so that they may serve as donors toward free GeF_4 . This phenomenon of induced basicity is known for other halides. For example, BF_3 does not self-associate but upon coordination to pyridine the fluorines become sufficiently basic to bind another BF_3 at low temperatures (*i.e.*, $\text{py}\cdot\text{BF}_3\cdot\text{BF}_3$).³⁰

Charge-Transfer Spectra.—Comparison of the charge-transfer bands presented in Table III and Figure 2 reveals that for the 1:1 adducts these bands are shifted to higher energy in the series $\text{SiF}_4 < \text{GeF}_4 < \text{SnF}_4$.³¹ This order parallels the generally accepted order of acidity. It is also clear from Table III that except for the SnF_4 adducts the metal to ligand charge-transfer band is shifted to higher energies as the proportion of Lewis acid in the complex is increased. These shifts are much less dramatic than the shift found when comparing $\text{Fe}(\text{phen})_2(\text{CNBF}_3)\text{CN}$ with $\text{Fe}(\text{phen})_2(\text{CNBF}_3)_2$.² This difference is reasonable in view of the structures proposed for the group IV adducts in which both CN groups of the parent iron complex are in bridging environments for all ratios of acid to base. There are no significant differences between the charge-transfer spectrum of a group IV chloride adduct and the corresponding fluoride. This result was unexpected, since the fluoride is generally the stronger acid.

Acknowledgment.—This research was supported by funds from the N.S.F. (Grants GP-1977 and GP-3804) and from the Advanced Research Projects Agency of the Department of Defense through Northwestern University Materials Research Center. In addition, J. J. R. was the holder of a N.I.H. Fellowship throughout most of this work. We wish to thank Professor A. L. Allred for pure samples of group IV halides.

(29) However, there are strong analogies with $\text{Si}_6\text{Cl}_{14}\cdot\text{SiCl}_4$ and $\text{Si}_6\text{Cl}_{14}\cdot\text{SiHCl}_3$: A. Kaczmarezyk, J. W. Nuss, and G. Urry, *J. Inorg. Nucl. Chem.*, **26**, 427 (1964). Also, SnF_4 is polymeric.

(30) H. C. Brown, P. F. Stehle, and P. A. Tierney, *J. Am. Chem. Soc.*, **79**, 2020 (1957).

(31) Attempts to measure oxidation potentials of the adducts in methylene chloride solution were largely unsuccessful, due to adsorption of the complexes on the platinum electrode, also a stable reference potential could not be obtained in the presence of the complex. However, an indication was obtained that published correlation between oxidation potentials and charge-transfer spectra will hold for the MX_4 adducts because a methylene chloride solution of $\text{Fe}(\text{phen})_2(\text{CN})_2$ saturated with SiF_4 had charge-transfer absorption at $430\text{ m}\mu$ and a half-peak potential in the cyclic voltammogram at about 0.48 v more positive than the uncomplexed material. The correlation obtained for the boron adducts leads to the prediction that the half-peak potential should be 0.5 to 0.9 v from $\text{Fe}(\text{phen})_2(\text{CN})_2$ (ref 2).