Anal. Calcd. for $C_8H_9O_4NSnFe$: C, 26.86; H, 2.54; N, 3.92; Sn, 33.18; Fe, 15.61. Found: C, 27.12; H, 2.56; N, 4.10; Sn, 33.33; Fe, 15.53.

A portion of the nonvolatile oil was dissolved in ether and treated with 9 *M* sulfuric acid. The characteristic odor of iron carbonyl hydride became noticeable. When a solution of $[Ni(o\text{-phen})_3]Cl_2$ was added to an acetone solution of the oil, a voluminous yellow precipitate was formed. These reactions are used as qualitative tests for the presence of anionic iron carbonyl species.[10]

Acknowledgments.—The authors are grateful to the United States Office of Naval Research for generous support of this work which may be reproduced in whole or in part for any purpose of the United States Government. Thanks are due Dr. R. V. Parish for assistance in obtaining the infrared spectra and to Professor F. A. Cotton for helpful discussions.

CAMBRIDGE 39, MASSACHUSETTS

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[10] W. Hieber and G. Brendel, *Z. anorg. u. allgem. Chem.*, **289**, 324 (1957).

[CONTRIBUTION NO. 562 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Stereochemistry of Complexes Based on Metal Tetrafluorides

BY E. L. MUETTERTIES

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The general behavior of metal tetrafluorides toward a variety of organic donor molecules has been investigated. Most monofunctional donors formed octahedral complexes of the type $MF_4 \cdot 2$ donor, and in the case of the soluble TiF_4 and SnF_4 complexes, n.m.r. data showed them to have the donor atoms at positions *cis* to each other. Amides were found to complex through the carbonyl-oxygen atom. The tertiary amines were unpredictable in behavior forming either mono- or bis-amine complexes. The 1:1 amine complexes appear "polymeric" and are postulated to have octahedrally coördinated metal atoms through "fluorine bonding." Tendency to form 1:1 complexes is favored by the large steric requirements of tertiary amines and is enhanced if the metal fluoride is itself an associated compound. Silicon and germanium tetrafluorides appear to be much weaker acceptor molecules than TiF_4, SnF_4 and MoF_4, and in the case of the TiF_4 and SnF_4 complexes, rapid ($k \geqq 10^3$ sec.$^{-1}$) exchange of base occurs in solutions of the complexes in excess base at -25 to 25°.

Complexes of silicon tetrafluoride with certain organic donor molecules, *e.g.*, $N(CH_3)_3$, $HCON(CH_3)_2$ and complexes of titanium tetrafluoride with nitriles, ketones, alcohols and amines have been described. We have extended this chemistry with respect to the type of base and with respect to the fluoride. Fluorides investigated include TiF_4, ZrF_4, SiF_4, GeF_4, SnF_4, SF_4, TeF_4 and MoF_4. The major goals of this study were establishment of the general acceptor behavior of the metal tetrafluorides and determination of structure in these complexes.

Experimental

Reagents.—The tetrafluorides and tetrachlorides were obtained from commercial sources or were prepared by standard literature procedures. The gaseous tetrafluorides were purified by distillation; no purification procedure was used for the solid tetrafluorides.

Preparation of Complexes.—The SiF_4 and GeF_4 complexes were prepared by passing the gases into solutions of the base in ether, acetonitrile or benzene, and the complexes generally precipitated immediately from solution. The complexes were recrystallized from ether or acetonitrile. All of the complexes appeared to be decomposed rapidly by water or alcohols. Molecular weights in water decreased with time to fractional values in accord with observed changes, *e.g.*, silica precipitation or rapid decomposition.

ZrF_4 complexes were prepared by refluxing a slurry of the tetrafluoride in excess organic base and then filtration into a mixture of toluene and ether to precipitate the complex. No crystalline complexes were obtained by this approach with pyridine, acetone oxime and N,N,N',N'-tetramethylethylenediamine. Ethers, nitriles and sulfones did not react at 50–160° with ZrF_4.

Sulfur tetrafluoride reactions with a wide variety of organic bases were investigated in a vacuum train. The high solubility in these bases indicated complex formation, but the F^{19} spectra[1] of these SF_4 solutions gave no evidence of complex formation with the exception of $N(CH_3)_3$, $N(C_2H_5)_3$ and pyridine where, instead of the characteristic SF_4 resonance, a single F^{19} resonance was observed. Crude tensiometric studies indicated 1:1 proportion for the amine complexes in the case of pyridine and of triethylamine. The pyridine complex was significantly dissociated at 25°.

Two general methods for the preparation of TeF_4, MoF_4, TiF_4 and SnF_4 complexes were used: (1) Solution of MF_4 in tetrahydrofuran, dimethoxyethane or acetonitrile, filtration of the solution, and addition of the organic base or a solution of the base in an ether to the MF_4 solution. (2) Direct reaction of MF_4 and the base and isolation of the complex by concentration (solvent evaporation) to incipient crystallization or by vacuum removal of the excess base (a last resort that was necessary only for the TiF_4 complexes with ketones, alcohols and carboxylic acid). The relationship of the 1-propanol–TiF_4 system was established by tensiometric studies.

Pyridine–TiF_4 System.—The reaction of pyridine and titanium tetrafluoride was investigated in some detail. The only analytically pure product obtained, a 1:1 complex, was prepared by adding pyridine to a dilute solution of TiF_4 in dimethoxyethane. A precipitate formed immediately. The precipitate was filtered and washed at least six times with dimethoxyethane and with ether and then dried at $\sim$30° for 12 hr. The 1:1 complex when extracted (very slow process—12 hr. for 0.6 g. to be extracted) with refluxing pyridine yielded a white solid (no melting point) that by analysis was neither $TiF_4 \cdot py$ nor $TiF_4 \cdot 2py$ but of a composition intermediate between these two. Further washing with ether and vacuum drying of this solid led to a reduction in amine content. A solid that gave analysis and behavior similar to the extracted solid was obtained by adding a dilute dimethoxyethane solution of TiF_4 to a solution of pyridine in dimethoxyethane keeping the pyridine in large excess. This behavior suggests either that the 1:1 complex strongly adsorbs pyridine or that the 2:1 complex is significantly dissociated at room temperature. The latter explanation is the more probable, since Emeleus and Rao[3] report that their $TiF_4 \cdot 2py$ preparation has a dissociation pressure of about 3 mm. at $\sim$60°.

Miscellaneous Reactions.—Several base reactions deserve special comment. Trifluoroacetic acid proved to be the only "inert" solvent for TiF_4 in that TiF_4 could be recrystallized from the acid. 1,1,2,2-Tetrafluoroethanol dissolved TiF_4 without heat evolution but some slight irreversible reaction prevented complete recovery of TiF_4 from the solution. Tetramethylene sulfone also dissolved TiF_4 but no crystalline

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[1] E. L. Muetterties and W. D. Phillips, THIS JOURNAL, **81**, 1084 (1959).

product was isolated successfully. Solid TiF_4 when added to ethyl ether or to alkyl thioethers produced tarry oils and solids. Ethyl ether when distilled into a trap containing TiF_4 at −78° and allowed to warm to 25° produced a noncrystalline, tan solid that contained ~15% carbon as compared to calculated values of 35 and 24% for 2:1 and 1:1 complexes, respectively. Ammonia and protonic amines gave fluorotitanates when reacting with ethereal solutions of TiF_4; these results are not in agreement with those of Ruff and Ipsen[2] and of Emeleus and Rao.[3] The ether may have played a role in the dehydrofluorination.[4] Ruff and Ipsen did not use a solvent, and Emeleus and Rao report no experimental procedure.

Results

The analytical and physical data for the MF_4 and some MCl_4 (for comparison) complexes and for the β-diketone reaction products are listed in Tables I and II, respectively. The diketone reaction products are listed separately because they, in some cases, were simply complexes and, in others, were chelates (unstable to hydrolysis and alcoholysis) resulting from HF elimination. 8-Hydroxyquinoline, a common chelate former, gave only complexes (Table I).

Those complexes previously described in the literature are duly noted with the pertinent references. Several complexes reported in the literature and not prepared in this study also are listed for comparison. Melting points qualified with the "d" indicate dependency on rate of heating (indicative of decomposition) or visual evidence of decomposition not necessarily accompanied by complete melting.

Attempts were made by Mr. A. F. Biddle of this Laboratory to index the X-ray powder patterns of some of the complexes. The $TiF_4 \cdot 2(CH_3)_2NCHO$ complex was satisfactorily indexed on the basis of a tetragonal crystal: a_0 = 14.01 Å.; c_0 = 21.96 Å.; c/a = 1.567; z = 16; $d_{\text{calcd.}}$ = 1.664; $d_{\text{obsd.}}$ = 1.631. Reasonable agreement also was found for a tetragonal assignment for $TiF_4 \cdot 2(CH_3)_2SO$ (a_0 = 18.49 Å.; c_0 = 14.47 Å.; c/a = 0.7826; z = 16) but the observed density, 1.650, was much greater than the calculated density, 1.504.

Discussion

A. General.—Before discussing the results of this work, it is important to point out some general properties of the metal tetrafluorides. In the case of the tetrafluorides of Group IV elements, there are two different types: (1) the unassociated and highly volatile compounds (SiF_4 and GeF_4) and (2) the highly associated and relatively nonvolatile solids (SnF_4, TiF_4 and ZrF_4). The dividing line between these two classes is very sharp and appears at the first long period of the Periodic Table[5]; germanium tetrafluoride sublimes (760 mm.) at − 36° and tin tetrafluoride and the IV B tetrafluorides sublime or boil at temperatures ranging from 280–800°. This cannot be a discontinuous change in bond type from highly covalent to highly ionic although the *trend* from covalent to ionic undeniably exists. A similar, although not as sharp,[6] differentiation occurs in Group V tetrafluorides at MoF_4 in the second long period. It is suggested that this differentiation in physical properties is a reflection of the greater tendency of the heavier elements to achieve a maximum degree of coördination; in the case of the Group IV fluorides, this would be an octahedrally coördinated metal atom.[7] The behavior of these tetrafluorides as acceptor molecules also reflects these tendencies toward association and this point is discussed below. Without a detailed structural analysis of the solid tetrafluorides, the mode of association cannot be precisely described but for the purposes of this discussion the mode of association will be presented as metal-fluorine-metal interactions or "fluorine bonding."[8]

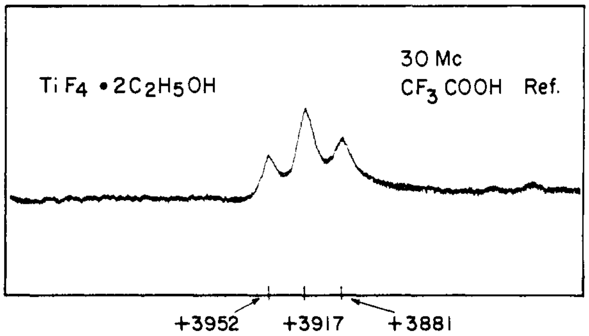

Fig. 1.—Partial F^{19} spectrum of ethanol solution of $TiF_4 \cdot 2C_2H_5OH$ at ~−20°. This is one of two triplets; the chemical shift is about 1760 c.p.s. The F–F coupling constant for this complex is 36 c.p.s. as compared to 37 and 39 c.p.s. for $TiF_4 \cdot 2(CH_2)_4O$ and $TiF_4 \cdot 2CH_3CON(CH_3)_2$, respectively.

B. Stereochemistry of the TiF_4 and SnF_4 Complexes.—For the most part, the formulation of

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[2] O. Ruff and R. Ipsen, *Ber.*, **36**, 1777 (1903).

[3] H. J. Emeleus and G. S. Rao, *J. Chem. Soc.*, 4245 (1958).

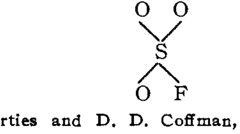
[4] Ethers can promote dehydrofluorination, *e.g.*, BF_3 and $RO(CH_2)_xNH_2$ form tetrafluoroborates in ether solvents but form adducts in the absence of ethers, *cf.* E. L. Muetterties, *Z. Naturforsch.*, **12b**, 264 (1957).

[5] It should be noted that this "dividing line" does not appear at this point for the tetrachlorides but rather with zirconoum in the second long period.

[6] SeF_4 (b.p. 93°) is, however, significantly more associated than SF_4 (b.p. ~−40°). Tendency towards association here may play arole in fluorine exchange, *cf.* E. L. Muetterties and W. D. Phillips, ref. 1.

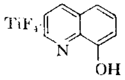
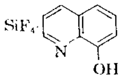
[7] Generally, "maximum covalency" is more readily achieved in fluorides than in chlorides. This is reflected even in the physical properties of the Group IV A fluorides and chlorides where there are sharp discontinuities in association for the fluorides but only a steady increase for the chlorides. Note the inversion in volatilities (b.p. in parentheses) of fluorides *versus* chlorides: SiF_4 (−96°) > $SiCl_4$ (57°), GeF_4 (−36°) > $GeCl_4$ (87°) and $SnCl_4$ (114°) > SnF_4 (>250°).

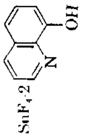
[8] "Fluorine bonding" is an established phenomenon. It has been rigorously established in hydrogen fluoride (but in this case, it is classically described as hydrogen bonding) and fairly conclusively in antimony pentafluoride (*cf.* C. A. Hoffman, B. E. Holder and W. L. Jolly, *J. Phys. Chem.*, **62**, 364 (1958) and E. L. Muetterties and W. D. Phillips, THIS JOURNAL, **79**, 3686 (1957)) and in



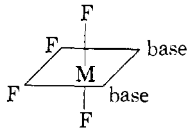
(E. L. Muetterties and D. D. Coffman, *ibid.*, **80**, 5914 (1958)). "Fluorine bonding" also has been hypothesized as a mode of association or fluorine exchange mechanism for a number of fluorides (E. L. Muetterties and W. D. Phillips, ref. 1, and H. C. Clark, *Chem. Revs.*, **58**, 869 (1958)).

TABLE I: COMPLEXES OF METAL TETRAHALIDES

	Compound	Calcd., %						Found, %						M.p., °C.	$d_0^{25°}$	Previous lit. ref.
		C	H	M	F(Cl)	N (S)	MW	C	H	M	F(Cl)	N (S)	MW			
TiF_4	$TiF_4 \cdot 2(CH_3)_2SO$	17.15	4.32	17.10	27.13	22.89	280.17	17.42	4.46	16.86	26.99	22.03	274^{THF}	182–184	1.650	
	$TiF_4 \cdot 2(CH_3)_2NCHO$	26.60	5.21	17.68	28.06	10.34	270.66	27.24	5.20	17.04	28.32	10.39	264^{CH_3CN}	202–203	1.631	
	$TiF_4 \cdot 2(CH_3)_2NC(CH_3)O$	32.23	6.09	16.07	25.49	9.40	298.14	32.98	6.35	15.87	24.99	9.34	300^{CH_3CN}	131–134	1.470	
	$TiF_4 \cdot 2[(CH_3)_2N]_2CO$	33.72	3.98	13.45	21.34	15.73	356.22	32.96	6.04	12.79	21.68	15.54	266^{CH_3CN}	100–110 d.	...	
	$TiF_4 \cdot 2(CH_3)_2C{=}NOH$	26.60	5.21	17.68	28.06	...	270.56	26.04	5.21	17.68	27.57	...	189^{THF}	.....	...	
	$TiF_4 \cdot CH_3CN$	14.56	1.83	29.04	46.07	...	164.95	13.79	2.35	28.45	45.62	...	173^{THF}	60–63	1.478	3
	$TiF_4 \cdot (CH_3)_3N$	19.69	4.96	26.17	41.53	7.65	183.01	18.97	4.48	26.95	40.03	6.17	.....	>350	...	
	$TiF_4 \cdot C_5H_5N$	29.58	2.48	23.60	37.44	...	203.00	29.94	2.92	23.70	38.96	...	.....	>360	1.923	2
	$TiF_4 \cdot 2,4\text{-}(CH_3)_2C_5H_3N$	36.39	3.93	20.73	...	6.06	231.05	37.07	4.10	20.29	...	6.98	.....	>200	...	
	$TiF_4 \cdot C_6H_5(CH_3)_2N$	...	..	19.55	...	5.72	245.08	...	..	20.54	...	5.71	298^{CH_3CN}	57–59	...	
	$(TiF_4)_4 \cdot [(CH_3)_2N]_4C_2$	17.26	3.48	27.53	43.68	8.05	695.91	18.23	4.05	26.58	42.02	7.14	.....	175 d.		
	$TiF_4 \cdot [(CH_3)_2NCH_2CH_2N(CH_3)_2]$	30.01	6.72	19.94	...	...	240.102	28.69	6.92	19.05	...	...	.....	270–300 d.	...	
	$TiF_4 \cdot C_2H_5N(CH_2CH_2)_2O$	30.14	5.48	20.04	...	...	239.07	31.21	6.44	19.50	...	...	.....	.....	...	
		...	..	16.80	26.66	4.91	285.05	...	..	16.88	27.45	5.02	265^{CH_3OH}	220 d.	1.722	
	$TiF_4 \cdot 2(CH_2CH_2)_2O$	35.84	6.02	17.87	28.35	...	268.11	33.70	6.24	17.55	28.59	...	269^{THF}	.....	..	
	$TiF_4 \cdot O(CH_2CH_2)_2O$	22.66	3.80	...	35.85	...	211.97	23.09	4.16	...	34.12	...	205^{THF}	.....	...	
	$TiF_4 \cdot CH_3OCH_2CH_2OCH_3$	22.44	4.71	...	...	...	214.08	22.02	5.02	...	...	...	216^{THF}	.....	...	
	$TiF_4 \cdot 2C_3H_7OH$	...	..	...	...	...	216.04	($C_3H_7OH:TiF_4$ ratio = 1.97:1.00)						Oil	...	
	$TiF_4 \cdot 2CH_3COOH$	19.69	3.30	19.63	31.15	...	244.00	20.31	4.15	17.09	29.65	...	....	Oil	...	
	$TiF_4 \cdot 2CH_3COCH_3$	30.02	5.04	...	...	...	240.06	31.95	5.78	...	...	...	.....	Oil	...	
ZrF_4	$ZrF_4 \cdot 2(CH_3)_2SO$	14.86	3.74	28.21	23.50	19.83	323.49	14.20	4.01	28.15	...	18.63	.....	.....	...	
	$ZrF_4 \cdot [(CH_3)_2N]_2CO$	...	..	32.19	26.82	9.89	238.80	...	...	33.91	23.83	9.16	252^{CH_3CN}	.....	...	
	$ZrF_4 \cdot (CH_3)_2NCHO$	14.96	2.93	37.88	...	5.81	240.817	16.08	3.66	37.92	...	6.12	.....	.....	...	
	$ZrF_4 \cdot 2(4\text{-}CH_3C_5H_4N)$	40.77	3.99	...	...	7.93	353.47	40.52	4.67	...	...	7.11	.....	.....	...	
SiF_4	$SiF_4 \cdot 2(CH_3)_2SO$	18.45	4.65	...	29.19	24.63	260.36	18.52	4.91	...	28.26	24.55	265^{THF}	118	...	
	$SiF_4 \cdot 2(CH_3)_2NCHO$	29.03	4.87	11.31	30.61	11.28	248.26	29.00	5.70	10.67	29.14	11.45	.....	163–164	...	9
	$SiF_4 \cdot 2(CH_3)_2C{=}NOH$	29.03	4.87	11.31	30.61	11.28	248.26	28.29	5.73	11.85	28.34	11.20	.....	147–148	...	
	$SiF_4 \cdot 2C_6H_5(CH_3)_2N$	55.47	6.40	8.11	21.94	8.09	346.44	53.96	6.31	8.22	...	7.40	.....	.....	...	
		...	..	11.27	...	5.62	249.24	...	...	10.71	...	5.85	232^{H_2O} 182^{CH_3CN}	.....	...	
	$SiF_4 \cdot C_5H_5N$	32.78	2.75	15.34	...	...	183.19	33.00	3.42	15.35	...	...	.....	.....	...	
	$SiF_4 \cdot [2,4\text{-}(CH_3)_2C_5H_3N]$	39.80	4.29	...	...	6.63	211.24	42.26	5.36	...	...	7.36	.....	.....	...	
	$SiF_4 \cdot 2(CH_3)_3N$	Ref. 9														10
	$SiF_4 \cdot (CH_3)_3N$	Ref. 10														10
GeF_4	$GeF_4 \cdot 2(CH_3)_2SO$	15.76	3.97	23.81	...	21.04	304.87	15.14	3.83	22.14	...	20.22	81^{H_2O}	>250	1.893	
	$GeF_4 \cdot 2(CH_3)_2HCHO$	24.44	4.79	...	25.78	...	294.79	24.65	4.72	...	24.50	...	92^{H_2O}	>250	1.825	
	$GeF_4 \cdot 2(CH_3)_2C{=}NOH$	24.44	4.79	...	25.78	...	294.79	25.49	4.98	...	24.71	...	91^{H_2O}	200 d.	1.830	
	$GeF_4 \cdot 2C_5H_5N$	39.15	3.29	...	...	9.13	306.79	40.20	4.09	...	...	10.62	.....	.....	...	
	$GeF_4 \cdot 2(CH_3)_2NC_6H_5$	49.15	5.67	...	...	7.17	390.95	48.41	6.30	...	...	7.19	.....	.....	...	

SnF_4	$SnF_4 \cdot 2(CH_3)_2SO$	13.69	3.45	33.82	. . .	18.27	350.97	13.26	3.48	34.20	. . .	16.44	344^{THF}	. . . . .	. . .	
	$SnF_4 \cdot 2(CH_3)_2NCHO$	21.14	4.14	34.82	22.29	8.22	340.89	21.05	4.16	34.45	21.50	8.20	312^{THF}	. . . . .	. . .	
	$SnF_4 \cdot 2[(CH_3)_2N]_2CO$	28.13	5.67	27.80	. . .	13.12	427.02	27.75	5.86	27.78	. . .	13.20	. . . .	. . . . .	. . .	
	$SnF_4 \cdot 2(CH_3)_2C{=}NOH$	21.14	4.14	34.82	22.29	8.22	340.89	. . .	. .	. . .	. . .	. . .	. . . . .	160 d.	. . .	
	$SnF_4 \cdot 2C_5H_5N$	34.03	2.86	33.64	. . .	7.94	352.89	32.09	3.64	30.02	. . .	7.22	. . . . .	180–183	. . .	
	$SnF_4 \cdot [4\text{-}CH_3C_5H_4N]$	. . .	. .	. . .	. . .	4.87	287.82	. . .	. .	. . .	. . .	4.43	. . . . .	. . . . .	. . .	
	$SnF_4 \cdot [2,4\text{-}(CH_3)_2C_5H_3N]$	. . .	. .	. . .	. . .	4.64	301.85	. . .	. .	. . .	. . .	5.47	. . . . .	. . . . .	. . .	
	$SnF_4 \cdot 2$ 	44.57	2.91	. . .	. . .	5.78	485.01	45.17	3.77	. . .	. . .	5.78	. . . . .	. . . . .	. . .	
MoF_4	$MoF_4 \cdot 2(CH_3)_2SO$	14.64	3.69	29.23	. . .	19.54	328.22	15.28	3.84	28.81	. . .	20.22	. . . . .	. . . . .	. . .	
	$MoF_4 \cdot 2(CH_3)_2NCHO$	22.65	4.44	30.16	. . .	8.81	318.14	23.03	4.72	30.98	. . .	8.91	. . . . .	. . . . .	. . .	
	$MoF_4 \cdot C_6H_5N(CH_3)_2$	32.78	3.78	32.73	. . .	4.78	293.13	33.41	4.20	31.28	. . .	4.54	. . . . .	. . . . .	. . .	
	$MoF_4 \cdot C_5H_5N$	36.37	3.05	29.06	. . .	8.49	330.15	35.66	3.57	28.88	. . .	8.26	. . . . .	~210 d.	1.739	
	$MoF_4 \cdot N(CH_3)_3$	. . .	. .	33.06	. . .	9.65	290.17	. . .	. .	31.09	. . .	9.50	. . . . .	~180 d.	1.739	
MCl_4	$TiCl_4 \cdot 2(CH_3)_2NCHO$	21.45	4.20	. . .	42.22	8.34	335.91	22.12	4.64	. . .	42.33	8.52	. . . . .	. . . . .	. . .	11
	$TiCl_4 \cdot 2(4\text{-}CH_3C_5H_4N)$	38.33	3.75	. . .	. . .	7.45	375.97	37.57	4.60	. . .	. . .	7.45	. . . . .	. . . . .	. . .	
	$TiCl_4 \cdot (CH_3)_3N$	Ref. 12														12
	$SnCl_4 \cdot 2(CH_3)_3N$	Ref. 13														13
	$SnCl_4 \cdot 2(CH_2)_4O$	Ref. 14														14
	$ZrCl_4 \cdot 2CH_3CN$	Ref. 3														3
	$SiCl_4 \cdot 2C_5H_5N$	Ref. 9, 15														9,15

the Group IV tetrafluoride complexes is that of two molecules of base to one molecule of fluoride unless, of course, the base is di- or poly-functional. This is fully consistent with an expected octahedrally coördinated central metal atom; octahedral coördination has been well established for the hexafluoride anions of several of these elements, *e.g.*, $SiF_6^{=}$,[1,15a] $GeF_6^{=}$[15b] and $PbF_6^{=}$.[17] The F^{19} magnetic resonance spectra of most of the soluble 2:1 (or 1:1 where the base is difunctional) titanium and tin complexes gave fairly conclusive evidence for octahedral symmetry and for a preferred stereochemistry. At temperatures of about +15° down to the freezing point of the solvent, solutions of these complexes in ethers, nitriles or simply excess base consisted of two resonances of equal intensity, each of which was split into triplet structures (Fig. 1). This is indicative of two types of fluorine environment that have equivalent populations. The only structure[18] consistent with the spectra is an octahedral model in which the base molecules occupy positions *cis* to each other.



Because of the seemingly bulky nature of the base ligands, a *cis* structure would appear less likely than a *trans* structure. However, molecular models were made of all those types of base complexes that generally show 2:1 proportion, and no significant differences between the *cis* and *trans* structures were apparent from the standpoint of steric repulsions. There was one exception: very large steric repulsions were apparent in amide complexes based on models with metal–nitrogen coordination. However, in the models based on metal–oxygen (carbonyl) coördination, there were no significant problems. The 2:1 proportion of the tetramethylurea complex with TiF_4 suggests oxygen coördination. Conclusive evidence for oxygen coördination was found in the infrared spectra of the amide complexes.[19] The carbonyl band in these complexes is shifted (50–80 cm.$^{-1}$) to lower wave numbers. Furthermore, *cis* con-

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(14) S. T. Zenchelsky and P. R. Segatto, *ibid.*, **80**, 4796 (1958).

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(16) (a) Y. K. Syirkin and M. V. Volkinstein, *Acta. Physicochim. U.R.S.S.*, **2**, 308 (1935); (b) J. L. Hoard and W. B. Vincent, THIS JOURNAL, **62**, 3126 (1940).

(17) R. Hoppe and K. Klinne, *Z. anorg. u. allgem. Chem.*, **293**, 251 (1958).

(18) A trigonal prism with base molecules at *trans* positions on a square or rectangular face would have two equally populated fluorine environments. But because F–F bond angles would not be identical here and, accordingly, the coupling (F–F) constants should be different, this is a highly improbable structure.

(19) Probably most amide complexes are based on oxygen coördination. In a number of cases, nitrogen coördination has been cited but these cases should be reinvestigated. Reinvestigation of the BF_3 amide complexes shows the original assignment (*cf.* E. L. Muetterties and E. G. Rochow, THIS JOURNAL, **75**, 490 (1953)) of B–N coördination is incorrect.

TABLE II

DIKETONE REACTION PRODUCTS WITH MX_4

			Analytical										
			Calcd.					Found					
Halide	Ketone	Product MX_4:ketone	C	H	M	X	MW	C	H	M	X	MW	M.p.
SiF_4	$CH_3COCH_2COCH_3$	Very weak complex (25°)	...	..	...	...	....	...	..	...	...	.....	....
SiF_4	Tropolone	(1:2)–2HF	54.18	3.90	9.05	12.24	310.33	54.38	3.34	8.74	12.93	.....	....
GeF_4	$CH_3COCH_2COCH_3$	Very weak complex (25°)	...	..	...	...	....	...	..	...	...	.....	....
SnF_4	$CH_3COCH_2COCH_3$	Complex (25°)	...	..	...	...	....	.....	..	...	...	.....	....
SnF_4	Tropolone	(1:2)–2HF	42.14	2.53	...	...	398.94	43.70	2.77	...	...	.....	....
TiF_4	$CH_3COCH_2COCH_3$	(1:2)–2HF	42.27	4.97	16.86	13.38	284.11	42.96	5.01	16.28	14.26	.....	124 d.
TiF_4	$C_6H_5COCH_2COCH_3$	(1:2)–2HF	...	..	11.73	9.31	408.24	...	..	11.56	9.78	216^{EtOH}	195–199 d.
TiF_4	Tropolone	(1:2)–2HF	51.24	3.07	14.60	...	328.12	51.76	3.37	14.21	...	.....	....
ZrF_4	$CH_3COCH_2COCH_3$	No reaction (60°)	...	..	...	...	....	...	..	...	...	.....	....
MoF_4	$CH_3COCH_2COCH_3$	Very air-sensitive, yellow solid	...	..	...	...	....	...	..	...	...	.....	....
$SiCl_4$	$CH_3COCH_2COCH_3$	(1:3)–3HCl	Ref. 20										
$SnCl_4$	$CH_3COCH_2COCH_3$	(1:2)–2HCl	30.97	3.64	30.61	18.29	387.83	31.35	4.07	...	19.42	.....	240 d.
$TiCl_4$	$CH_3COCH_2COCH_3$	(1:2)–2HCl	Ref. 21										

figurations for $TiF_4 \cdot 2(CH_3)_2NC(CH_3)O$ and $TiF_4 \cdot 2(CH_3)_2NCON(CH_3)_2$ were established by the F^{19} resonance spectra of solutions of these complexes. The $TiF_4 \cdot 2(CH_3)_2NCHO$ complex was too insoluble for solution n.m.r. studies.

C. Ligand Exchange.—The F^{19} spectra of the solutions of the TiF_4 and SnF_4 complexes in ethers or in excess base were temperature dependent. On warming these solutions, the fine structure of the F^{19} spectrum is lost, the peaks broaden and then collapse into a single resonance. This is characteristic of an exchange process (order of magnitude of exchange rate is about 10^3 sec.$^{-1}$ at $0 \pm 30°$). Since in these solutions the base is in excess and since thermal tensiometric studies established base dissociation,[22] this must be an exchange of base molecules. Recooling of the solutions of the complexes reversibly yields the low temperature F^{19} spectra. Thus, the *cis* structure *appears*[23] to be thermodynamically favored suggesting that repulsions between fluorine atoms and base molecules are structure determining.[24]

The F^{19} spectra of all the SiF_4 and GeF_4 complexes consisted of single fluorine resonances from the freezing points of the solutions to temperatures well above room temperature. This could indicate preferential *trans* formation; however, it is not conclusive because absence of fine structure, indicative of *cis* structures, could be due to fast ligand exchange. Fast ligand exchange is likely in that the GeF_4 and SiF_4 complexes are much more highly dissociated in accord with the previously postulated, lesser tendency of these tetrafluorides toward achieving "maximum covalency." For example, SiF_4 and GeF_4 neither evolve significant heat when mixed with ketones, ethers or nitriles nor form isolable complexes, yet TiF_4 and SnF_4 react exothermally with these bases to give isolable complexes. With this order of magnitude difference in stability and with an approximate exchange rate of 10^3 sec.$^{-1}$ in the TiF_4 and SnF_4 complexes at $0 \pm 30°$, it is not unexpected for fine structure to be absent in the spectra of the SiF_4 and GeF_4 complexes.

D. "Polymeric" Complexes.—The metal tetrafluorides, particularly TiF_4 and SnF_4, displayed a *tendency* to form 1:1 complexes with tertiary amines and with nitriles. The $TiF_4 \cdot CH_3CN$ complex behaves as a molecular complex in that it is low melting and readily soluble in excess nitrile or ethers. The molecular weight of the complex in these solutions corresponds to a monomer but this does not necessarily imply a pentacovalent complex in that base solvent can (and undoubtedly does) occupy the sixth site of the octahedron and this would not detectably affect the molecular weight value. Acetonitrile solutions of the complex display an F^{19} spectrum identical to the 2:1 complexes described above. The F^{19} spectrum is explainable on the basis that a 2:1 ratio exists in solution in excess base. The solid complex may be a dimer (or cyclic trimer or tetramer) based either on CN or fluorine bridging. In view of the known tendency of CN to bridge and of the striking difference in physical properties between this complex and the amine complexes discussed below, CN bridging seems the more likely explanation.

The 1:1 amine complexes of TiF_4 are rather unexpected since the amines are much more basic than, for example, the ethers which form 2:1 complexes. However, molecular models indicated possible steric repulsions in 2:1 trialkylamine complexes. In fact, models of the presumably favored *cis* structure could not be made. Models did indicate that *cis* structures were possible with the bidentate N,N,N′,N′-tetramethylethylenediamine ligand and we were successful in isolating such a complex in the case of TiF_4.

The 1:1 amine complexes are significantly different from the 2:1 complexes and the 1:1 nitrile complex in physical and chemical properties.

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[20] W. Dilthey, *Ber.*, **36**, 923 (1903).

[21] K. C. Pande and R. C. Mehrota, *Chem. & Ind.* (*London*), 1198 (1958).

[22] Furthermore, intermolecular fluorine exchange in octahedral MF_6, MF_6^- and $MF_6^=$ species is generally not observed under moderate conditions of temperature (50°); *cf.* ref. 1.

[23] In some cases, a third peak was observed that may have represented the *trans* form; however, this was attributed to impurities because the intensity of the peak was variable from preparation to preparation.

[24] *Cis* structures appear to be present also, at least to significant degrees, in metal tetrachloride complexes. O. A. Osipov and V. B. Kretenik (*J. Gen. Chem. U.S.S.R.* (*Eng. Transl.*), **27**, 2953 (1957)) showed that the $ZrCl_4$ complexes with esters of carboxylic acids have very high dipole moments, 4–8 *D*, indicative of *cis* structures. Similarly, the $SnCl_4 \cdot 2ROOH$ complexes have high dipole moments and may be assumed to have, at least largely, the *cis* structure (O. A. Osipov, G. S. Samofalova and E. I. Glushko, *ibid.*, **27**, 1502 (1957)).

None of these 1:1 complexes has a sharp melting point; in fact, for the most part, they do not melt below 300° although most of them show signs of decomposition below this temperature. These complexes are relatively intractable; they have very little solubility in polar, nonprotonic solvents. Protonic solvents such as water and alcohols rapidly dissolve and decompose these complexes with deposition of colloidal TiO_2 and SnO_2 in a matter of seconds to minutes depending upon the particular complex. In contrast to this behavior $TiF_4 \cdot 2(CH_3)_2SO$ can be recrystallized from water without any evidence of decomposition, and $TiF_4 \cdot 2(CH_3)_2NCHO$ can be recrystallized from water with only slight decomposition.

The physical properties of the amine complexes, *i.e.*, absence of sharp melting points and the intractability, certainly indicate that they are not molecular, pentacovalent complexes but rather that they are polymeric complexes. Octahedral coördination could be preserved in a polymeric complex through "fluorine bonding."[25] This type of polymeric complex is wholly consistent with the reactivity toward protonic substances. An analogy may be drawn to illustrate this point. Antimony pentafluoride has octahedral coördination[17] in the liquid state through "fluorine bonding" and may be considered formally analogous to the 1:1 amine complexes. The hexafluoroantimonate anion also has octahedral coördination but, of course, no fluorine bridge bonds and may be considered formally analogous to a 2:1 MF_4 complex, *e.g.*, $TiF_4 \cdot 2(CH_3)_2SO$. Both SbF_6^- and $TiF_4 \cdot (CH_3)_2SO$ have the central atoms well shielded by negative substituents from nucleophilic attack and, accordingly, are not attacked readily by water. The central atoms in $(SbF_5)_x$ and the 1:1 amine complexes are similarly protected but the fluorine bridge bonds serve as reactive sites as witness the violent reaction of $(SbF_5)_x$ and water and the facile hydrolysis of the 1:1 amine complexes.

E. Complexes of Group VI Fluorides.—In the case of the Group VI tetrafluorides, the only complexes of any stability were those of MoF_4. Sulfur tetrafluoride is a very weak acceptor molecule, and although there is a heat of reaction or solution with many bases such as ethers and amides, only tertiary amines proved sufficiently basic to perturb the characteristic F^{19} resonance spectrum of SF_4. The F^{19} spectra of the amine SF_4 solutions consisted of single resonances and were essentially temperature ($\sim -100°$ to $+50°$) insensitive. Tellurium tetrafluoride reacted exothermally with a number of bases but secondary reactions occurred before the complexes could be isolated in pure form. With the exception of a very bulky amine $[C_6H_5N(CH_3)_2]$, the composition of the MoF_4 complexes is two molecules of base to one of MoF_4. The complexes are not paramagnetic, thus the non-bonding electrons are either in a pure *s* orbital or are involved in the hybridization of the molecule. Since there are no established instances of fluorine compounds in which non-bonding electrons are in pure *s* orbitals, the $MoF_4 \cdot 2$ base complexes are probably isostructural with IF_7 or TaF_7^-. The F^{19} resonance of solutions of these complexes consisted of a broad, single peak.

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WILMINGTON, DELAWARE

[25] Amine bridging is another possibility but in view of the association present in the parent fluorides, fluorine bonding seems more likely.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Reaction of Dithiol with Molybdenum

BY T. W. GILBERT, JR.,[1] AND E. B. SANDELL

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The reaction of molybdate in mineral acid solution with dithiol (H_2Di) gives a green complex in which the dithiol/molybdenum ratio is 3 and molybdenum is sexivalent, as shown by reacting ratios and magnetic susceptibility measurement. Its composition is probably $MoDi_3$. When molybdenum(V) reacts with dithiol in acid medium, disproportionation occurs and a quadrivalent red complex, probably to be formulated as $Mo^{IV}\ Di_2(H_2Di)$ or $Mo^{IV}\ Di(HDi)_2$, is formed in addition to the sexivalent green complex. Because of side reactions, the two complexes are usually not formed in equivalent amounts. Observations on the rate of reaction and equilibrium in the system Mo(VI)–dithiol are recorded.

Toluene-3,4-dithiol (4-methyl-1,2-dimercaptobenzene), commonly called dithiol, reacts with molybdate in acid solutions to give a slightly soluble green product, whose composition has not been established, which dissolves in various organic solvents immiscible with water.[2] The present paper deals with this reaction and also that between dithiol and molybdenum(V).

Molybdenum(VI)–Dithiol Reaction

Experimental

Materials.—A 0.1 *M* solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in water was standardized gravimetrically by precipitation as silver molybdate and stored in a paraffin-coated bottle.

Dithiol (L. Light and Co., Colnbrook, England) was dissolved in a slight excess of sodium hydroxide solution which had been deaerated with nitrogen. The storage bottle was sealed with a rubber self-sealing serum bottle cap and solution was withdrawn by means of a hypodermic syringe. The strength of the solution ($\sim 0.5\%$) was determined by amperometric titration with silver nitrate; iodimetric titration gave the same results. Three lots contained 87.6, 94.9 and 95.7% of the active reagent. Purification was not

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[1] This paper is based on the Ph.D. Thesis of T. W. Gilbert, Jr., University of Minnesota, 1956.

[2] (a) J. H. Hamence, *Analyst*, **65**, 152 (1940); (b) C. C. Miller and A. J. Lowe, *J. Chem. Soc.*, 1258 (1940); (c) J. E. Wells and R. Pemberton, *Analyst*, **72**, 185 (1947); (d) H. G. Short, *ibid.*, **76**, 710 (1951).