ADDITION COMPOUNDS OF THE GROUP IV HALIDES

I. TRIETHYLAMINE AND THE TETRACHLORIDES OF SILICON, GERMANIUM, TIN, AND TITANIUM[1]

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ABSTRACT

Compounds with the composition of tetraminates were prepared from the tetrachlorides of silicon, germanium, tin, and titanium with triethylamine. Thermal decomposition of the tetraminates leads to the suggestion that they are molecular addition compounds.

The existence of complex 'addition' compounds involving some group IV tetrahalides has been known for many years. Although these compounds present a specific challenge to valence theory, their existence has not been emphasized but rather seems to have been ignored or forgotten until recent time. Of the group IV*b* tetrachlorides (carbon, silicon, germanium, tin, lead), lead (5) and particularly tin (6) are known to form a variety of addition compounds with donor groups like ethers, ketones, aldehydes, and amines. Compound formation between silicon tetrachloride and pyridine, $SiCl_4 . 2Pyr$, was reported in 1887 (1), and between triethylamine and germanium tetraiodide in 1933 (3).

But much greater interest has been shown in the substitution reactions that silicon and germanium tetrahalides undergo, to form covalent compounds, than has been directed to addition type reactions that may simultaneously occur. The best condition for substitution, and that generally studied, occurs when the donor group is associated with reactive hydrogens. In this situation addition reactions can become obscured or even remain unnoticed. But when attention is focused on addition rather than on substitution, and conditions favorable to the formation of addition compounds are established, then evidence for such compounds can be discovered in the reactions of silicon tetrachloride with donor groups like aldehydes, ketones, and especially amines (10).

The remaining member of the group, carbon tetrachloride, does not easily engage in substitution reactions, nor is it by any means so adept at addition as are the heavier members of the family. However freezing point investigations have provided evidence for what seem to be definite, though low temperature, associations between carbon tetrachloride and pyridine (4).

The group IV*a* elements (titanium, zirconium, hafnium) could be expected to form complex compounds from their tetrahalides, for valence theory assigns to these atoms vacant *d* and *p* orbitals that can be used in conjunction with the donor electron pairs to establish orthodox coordinate bonds. Examples of known addition compounds are, however, rather limited, but the tetrachlorides of titanium and zirconium have recently been shown to be able to form compounds with organic esters (2).

The group IV*b* tetrahalides are saturated molecules in the sense that all orbitals

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and electrons in the valence group are fully engaged. This is in contrast to the group IV*a* tetrahalides, which still retain five vacant orbitals similar in stability to those utilized in the covalent bonding. If the valence orbitals are called 'n' type orbitals, then the group IV*a* tetrahalides will be able to form addition compounds with n type orbitals. But the group IV*b* tetrahalides must use $n + 1$ type orbitals, external to the valence group, if the additionlike compounds are to be interpreted in terms of coordinations (8).

Two questions of interest arise then, in regard to these compounds. First of all, are the addition compounds formed by the group IV*b* elements to be taken seriously as coordination compounds? If they are coordination compounds, the utilization of $n + 1$ type orbitals must also be taken seriously, with some general consequences in the fields of intermolecular forces, and of the structures of active complexes. Secondly, is there a distinctive difference between the addition compounds of the group IV*b* and the group IV*a* elements, corresponding to their different electron structures? With these particular problems in mind, some reactions of silicon, germanium, tin, and titanium tetrachlorides with triethylamine, and with ethylamine (11), were undertaken, and the results are presented and discussed below.

EXPERIMENTAL

Four tetrachlorides (silicon, germanium, tin, titanium) were each mixed with triethylamine under two different sets of conditions. In one series the compounds were prepared in vacuum with no solvent. In the other series reaction was effected in an anhydrous solvent in an atmosphere of dried nitrogen.

Vacuum Preparations

The amine and the tetrachloride were each prepared for use by two successive fractionations within the vacuum system. Known volumes of the purified liquids were condensed into a bulb at − 78°C., with the amine in 8/1 molar excess. The mixture was slowly warmed to room temperature while being magnetically stirred. All products volatile at 20°C. were pumped off and the dry products weighed and analyzed. The yields and compositions of the products are presented in Table I.

TABLE I

PREPARATIONS IN VACUUM
TRIETHYLAMINE AND GROUP IV TETRACHLORIDES

Tetrachloride	Product	Yield, %
$SiCl_4$	$SiCl_4.4NEt_3$	27
$GeCl_4$		8
$SnCl_4$	$SnCl_4.2NEt_3$	87
$TiCl_4$	$2TiCl_4.NEt_3$	80

The following observations on the vacuum preparations were thought to be significant. The mixtures of the amine with the tetrachlorides of silicon, germanium, and tin were white suspensions at low temperatures, with some yellow coloration that faded on warming in the case of silicon and germanium, but that became more extensive with time in the case of tin. Upon evaporation a white powder with the approximate composition, $SiCl_4 . 4NEt_3$, (Exp. Si, 4.7%; amine/Cl ratio, 1.06. Theor. Si, 4.9%; amine/Cl ratio, 1.00) was recovered from the silicon preparation. The germanium compound, in the process of evaporation, partly reverted to a yellow oily material that appeared as a contaminant in the white powder. The yield, Table I, was calculated in terms of a tetraminate. The tin compound was recovered as a yellow diaminate, $SnCl_4. 2NEt_3$ (Exp. Cl, 35.5%; NEt_3, 42.8%. Theor. Cl, 32.7%; NEt_3, 43.6%). The diaminate melted to a brown liquid in a 3° range at 75°C., and transformed slowly to the white and less dense tetraminate in liquid triethylamine at 20°C. The process of evaporation will affect the mole ratios in the tetrachloride–amine mixtures for, as judged by yields, conversion to the nonvolatile solids was by no means quantitative. The liquid condensates recovered while drying the silicon and germanium mixtures were yellow tinted solutions at − 78°C., but on warming towards 20°C. white suspensions again developed. The process was repetitive. In addition, oxygen gas had a definite effect on the silicon tetrachloride – amine mixtures, gas being absorbed with the simultaneous formation of a brown precipitate. Nitrogen gas had no effect on any of the preparations.

The behavior of the titanium tetrachloride – amine mixture in the vacuum preparation was in contrast to that of the group IV*b* elements. On warming from − 78°C. an intense red color spread in the amine as the frozen tetrachloride began to melt, but this disappeared abruptly when a quick spattering reaction produced a hard black solid. The latter substance had the approximate composition, $2TiCl_4. NEt_3$ (Exp. Cl, 58.5%. Theor. Cl, 58.5%). However, its aqueous acid solutions were red and its basic precipitates blue to violet, color reactions usually associated with Ti(+ 3) rather than Ti(+ 4).

Solvent Preparations

The solvent used was 30–60 petrol ether, dehydrated with sodium wire; 100 ml. of 0.2 molal tetrachloride solution added at the rate of 2 ml. per min. were magnetically stirred into 300 ml. of 1 molal triethylamine solution at 20°C. in an atmosphere of dried nitrogen. The apparatus had previously been dried at 120°C. The products formed as thick white suspensions and precipitates, and, after being washed in petrol ether, were filtered with the aid of rubber dams and dried in vacuum. The experimental yields, based on the tetrachlorides, varied from 50% to 75% for silicon, and from 85% to 100% for germanium, tin, and titanium.

Silicon and titanium were measured as the dioxides after slow ignitions. Chlorine and triethylamine were determined volumetrically (9). Substantial ignition losses with germanium and tin compelled the use of a wet method for determining them. They were measured as the dioxides, recovered from the digestion of the corresponding tetraminates in concentrated nitric acid. Tin was also separately determined* by means of the organic reagent, N-benzoylphenylhydroxylamine, confirming and improving on the metastannate analyses. The

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**Professor Ryan, Dalhousie University, who did the N-benzoylphenylhydroxylamine analyses, will publish the details of this method shortly.*

analytical results are presented in Table II, calculated on the basis of the assumed formula in column 1. Experimentally, the compounds conform to the tetraminate representation agreeably enough except in the case of titanium, where the mole ratio of amine to tetrachloride is 4.5 rather than 4.

TABLE II

ANALYSES OF THE AMINATES

Compound	Analytical composition, moles/mole aminate		
	M*	Cl	NEt_3
$SiCl_4.4NEt_3$	0.99	3.89	3.94
$GeCl_4.4NEt_3$	0.95	3.90	3.92
$TiCl_4.4NEt_3$	0.93	3.76	4.12
$SnCl_4.4NEt_3$	0.99	4.14	4.00
$SnCl_4.3NEt_3$	1.00	3.88	2.90
$SnCl_4.2NEt_3$		4.08	1.96
$SnCl_4.NEt_3$		4.03	0.99
$2TiCl_4.NEt_3$		8.00	

*M *is Si, Ge, Sn, or Ti.*

Two items in Table II require comment. The 'triaminate' of tin tetrachloride was a solvent preparation, but mixing occurred at 0°C., rather than 20°C. It was not possible to decide from the present work whether this was a real compound, or whether it was only a fortuitous combination of the di- and tetraminates. Another compound, the monaminate of tin tetrachloride, was prepared by adding triethylamine to excess tin tetrachloride. The product was a hard, dark, deliquescent solid, quite unlike the powdery di- and tetraminates.

Thermal Decomposition of the Tetraminates

The thermal decompositions were carried out in vacuum. Approximately 0.5000 gm. of the compounds were weighed out into a long tube that was then connected to a system containing a manometer and a trap. After thorough evacuation at room temperature the lower part of the tube, which contained the powder, was heated in an oil bath. All of the tetraminates developed vapor pressures of triethylamine on heating, and though these were not entirely independent of history and amount, the temperatures at which a vapor pressure of 20 mm. was created differentiated the tin tetraminate (ca. 65°C.) from the other three tetraminates (ca. 95°C.).

The amine was condensed into the trap at − 78°C. It was characterized by its vapor pressure, 20 mm. at 0°C., (7), and by analysis (back titrating a standard acid solution of the amine with a standard base, and then comparing the analytical weight with the gravimetric weight of the amine).

Another product, the hydrochloride of triethylamine, sublimed out of the decomposing reactant, and condensed as a solid on the walls of the cold part of the tube. The amine hydrochloride was characterized by determining the amine/Cl ratio, and by comparing analytic and gravimetric weights. Sodium fluorescein was the indicator in the titration for chloride with silver nitrate.

In preliminary runs it had been determined that the decomposition was a process which occurred in successive stages. On first heating a vapor pressure developed. If the volatile products were removed at 100°C. until the vapor pressure of the partially decomposed solid was reduced to about 0 mm., a second product appeared. Triethylammonium chloride, a subliming solid with no measurable vapor pressure at room temperature, began to appear when the silicon, germanium, and titanium compounds were still dry white powders; but the tin tetraminate residue was a brown liquid with the composition of the diaminate. Only a limited amount of triethylamine hydrochloride could be extracted from the decompositions at 100°C. The next step in the decomposition did not occur until the temperature was in excess of 135°C. Then the products became more complicated. The hydrochloride fraction became weight deficient compared to $Et_3N \cdot HCl$, a second component that was not an amine appeared in the volatile liquid product, and germanium and tin began to disappear from the decomposing residue.

The first two steps in the decompositions were then the evolution of triethylamine followed by the sublimation of the hydrochloride of triethylamine from the decomposing tetraminates. The yields of these two products, obtained at 100°C. in decompositions of one to two days duration, are listed for each of the four tetraminates in Table III. For each of the four compounds the sum of the two nitrogeneous products is almost equal to two moles of 'amine' per mole of tetraminate. That is, about one half of the amine contained in the tetraminate was removable at 100°C., and about one half was not. The form in which the amine appeared, however, whether as free amine or as the hydrochloride, varied considerably with the compound. For the compounds of silicon,* germanium, and titanium, the amine was preponderantly released in the form of the hydrochloride, although increasing amounts of triethylamine itself were recovered in the order silicon, germanium, titanium. Only in the decomposition of the tin tetraminate was triethylamine the major product. But when the tin tetraminate was decomposed at 150°C., the yield of triethylamine compared with the 100°C. decomposition was considerably reduced. It is to be noted that the amine hydrochloride recovered from the 150°C. decomposition had an experimental formula weight of 110 (column 5, Table III). The formula weight of triethylamine hydrochloride is 138.

TABLE III

THERMAL DECOMPOSITION OF THE TETRAMINATES

		Volatile products		
Tetraminate	Temp., °C.	Moles/mole tetraminate		Anal.g.F.W. $NR_3.HCl$
		Et_3N	$NR_3.HCl$	
$SiCl_4.4NEt_3$	100	0.1	1.8	138
$GeCl_4.4NEt_3$	100	0.4	1.8	137
$TiCl_4.4NEt_3$	115	0.8	1.5	
$SnCl_4.4NEt_3$	100	1.8	0.2	137
$SnCl_4.4NEt_3$	150	1.2	1.3	110

*The thermal decomposition of $SiCl_4.4Et_3N$ has been described before (9) but not in vacuum nor at constant temperature.

DISCUSSION

Three rather different explanations can be offered for the aminates of the group IV tetrachlorides. First of all, they may be thought of as ionic compounds, of the type $M(NEt_3)_4^{+4},4Cl^-$. Of the IV*b* tetrahalides, tin tetrachloride, because of the low electronegativity of tin, would be the chloride most easily ionized. But it is just this element whose non-ionic addition compounds are best known. If the three reactions for which evidence has been given are considered

$$SnCl_4 + 2Et_3N = SnCl_4.2Et_3N,$$
$$SnCl_4 + 4Et_3N = SnCl_4.4Et_3N,$$
$$SnCl_4.4Et_3N \underset{\text{rev.}}{=} SnCl_4.2Et_3N + 2Et_3N$$

and it is recalled that a coordination number of six is well known for tin, the assumption of ionic compounds for the aminates of the group IV halides becomes difficult to defend.

On the other hand it may legitimately be considered, particularly in the case of $SiCl_4.4NEt_3$, that the tetraminates merely correspond to mixtures of the hydrochloride of triethylamine with some substituted tetra-covalent compound of the group IV element. To correspond with the experimental data, however, this would require a low temperature decomposition of the tertiary amine, quantitative substitution of only two chlorines in the tetrachloride, and complete insolubility of both the hydrochloride and the substituted covalent compound in petrol ether. It is not very likely that even one of these restrictions could be fulfilled.

A remaining alternative is that the aminates of the group IV halides be interpreted as molecular addition compounds. The thermal decompositions are then to be understood as a competitive situation involving two reactions; first of all, the simple molecular dissociation liberating triethylamine; and secondly, the internal degradations leading to the formation of the hydrochloride of triethylamine. The large yield of triethylamine from the tin tetraminate is to be associated with the relative stability of the tin diaminate, and with the comparative inertness of tin tetrachloride towards substitution reactions. The small yields of triethylamine from the tetraminates of silicon, germanium, and titanium may conversely be related to the increasing strengths in coordinate bonding, and to greater substitutive reactivity in the halides. In either case, successive stages in the decompositions would be expected. When very little hydrochloride is released by the tetraminate, the steps would correspond to the evolution of two moles of amine followed by the different reaction, the decomposition of the diaminate. While, in the other extreme, if only triethylamine hydrochloride is obtained at first, when two moles of it are removed necessarily different degradations in a substituted compound would follow. However, the situation is not sufficiently simple to conclude that the strengths of the bonds between amine and tetrachloride decrease in the order silicon, germanium, titanium, tin as the vapor pressures and the amine/hydrochloride ratio otherwise suggest. Still, it can be decided that the tetraminate of titanium may be considered along with the tetraminates of the group IV*b* elements, silicon, germanium, and tin. And that the behaviors of these compounds are consistent with the assumption that they are molecular addition compounds.

To explain the molecular addition compounds of the group IV*b* tetrachlorides, it is necessary to assume that $n + 1$ type orbitals ((i.e., $(n + 1)s,nd$, $(n + 1)p$)) are functioning in the coordinate bonds that establish the compounds, whereas n type orbitals (i.e. ns, $(n - 1)d,np$) can be assigned to titanium tetrachloride. However, the proclivity of the two kinds of orbitals towards addition is not markedly different. That is, the electron structure of the group IV atom is not in itself decisive in establishing the stability of the vacant orbitals. If the orbitals are taken to be molecular, rather than atomic, then the contributions of the four chlorine atoms to the molecular orbitals, combined with the similar geometries of the molecules, will tend to make the different tetrachloride molecules more alike for purposes of addition. However, titanium is still not a regular member of the silicon, germanium, tin series, particularly in the distinctive compound $2TiCl_4 . NEt_3$.

The assumption of $n + 1$ type orbitals for the group IV*b* tetrachlorides may have some diagnostic value. For example, a consideration of the geometric and orbital factors in the group IV*b* tetrahalides leads to the conclusion that mono-, di-, tetra-, and hexaminates should be able to form as discrete addition compounds (8). Compounds corresponding to these four different ratios of amine to tetrachloride have been prepared. The mono-, di-, and tetraminates of tin tetrachloride with triethylamine have been reported above, and corresponding compounds between silicon tetrachloride and tertiary amines are known (8). In addition, the hexaminate of tin tetrachloride with ethylamine has been recently prepared (11).

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