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Spectrophotometric and Conductometric Studies on 2,2'-Bipyridyl Complexes of Some Tetravalent Silicon, Germanium and Tin Compounds in Acetonitrile

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Received March 5, 1969

Ultraviolet spectra and electric conductivities were measured for 2,2'-bipyridyl-$(CH_3)_3MCl$*(*$M=Si$*, Ge and Sn), –*$(CH_3)_2M'Cl_2$*(*$M'=Si$ *and Ge) and –*$(CH_3)_2SnX_2$*-(*$X=Br$ *and I) mixtures in acetonitrile. The results indicate that (i)* $(CH_3)_3SiCl$*,* $(CH_3)_2SiCl_2$ *and* $SiCl_4$ *form the 1:1, 1:2, and 1:3 complexes with 2,2'-bipyridyl, respectively, to give siliconium cations in solution, (ii)* $GeCl_4$ *exhibits the same behavior as* $SiCl_4$ *to give germonium cation, (iii)* $(CH_3)_3GeCl$*,* $(CH_3)_3SnCl$*, and* $(CH_3)_2SnBr_2$ *form non-ionic 1:1 adducts, and (iv)* $(CH_3)_2GeCl_2$ *and* $(CH_3)_2SnI_2$ *exist as equilibrium mixtures of the 1:1 and 1:2 complexes. For some of these complexes the stability constants in acetonitrile were also determined spectrophotometrically, and are discussed in comparing with those of 2,2'-bipyridyl complexes of* $SnCl_4$ *and* $(CH_3)_2SnCl_2$ *in solution.*

Introduction

The adducts of silicon(IV), germanium(IV) and tin(IV) compounds with nitrogen bases have widely been studied. For some of those, siliconium and germonium complex cations have been postulated in the solid state or in solution on the basis of infrared and ultraviolet spectra, and electric conductance; for instances, $[(C_6H_5)_3Si\cdot Bipy]^+I^-$ (where Bipy= 2,2'-bipyridyl),[1] $MI_4\cdot 2Bipy$($M=Si$[2] and Ge[3]), and $H_3SiX\cdot 2N(CH_3)_3$ ($X=Cl$, Br, and I).[4,5] Except for one of the latter complexes, however, it is little known that any adducts of silyl and germyl fluorides and chlorides and also tin halides ionize either in the solid state or in solution.

The present work was undertaken to see behavior of 2,2'-bipyridyl complexes of $M'Cl_4$, $(CH_3)_2M'Cl_2$ ($M'=Si$ and Ge), $(CH_3)_3MCl$ ($M = Si$, Ge, and Sn), and $(CH_3)_2SnX_2$ ($X=Br$ and I) in acetonitrile. A part of this work has briefly been described in the previous paper.[6] The stability constants of the complexes are compared with the previously reported ones for 2,2'-bipyridyl complexes of $(CH_3)_2SnCl_2$ and $SnCl_4$.

Experimental Section

Materials. Reagent grade 2,2'-bipyridyl was used without further purification, m.p. 70-72°C. $SiCl_4$ was obtained commercially and $GeCl_4$ was supplied from Germanium Information Center, Kansas, Missouri, U.S.A. These were purified by fractional distillation under dry nitrogen, b.p. 57.5°C and 83°C, respectively. $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$ supplied from Shin-etsu Chem. Co. Ltd. were carefully distilled through a Stedman column of about 20 plates, b.p. 58-59°C and 70.5°C, respectively. $(CH_3)_3GeCl$ (b.p. 98-99°C) and $(CH_3)_2GeCl_2$ (b.p. 124°C) were kindly supplied from Professor Kumada, Kyoto University. $(CH_3)_3SnCl$ was prepared by the usual redistribution reaction between $(CH_3)_4Sn$ and $(CH_3)_2SnCl_2$ in the presence of $SnCl_4$,[7] followed by fractional distillation, m.p. 38-39°C. $(CH_3)_2SnBr_2$ was obtained by the reaction of $(CH_3)_2SnO$ with HBr in aqueous solution,[7] and $(CH_3)_2SnI_2$ by the reaction of $(CH_3)_2SnCl_2$ with NaI in refluxing acetonitrile.[7] These were recrystallized from petroleum ether, m.p. 74°C and 43-44°C, respectively. Acetonitrile used for spectrophotometric and conductometric measurements was purified according to the literature,[8] λ at 25°C, 6×10^{-7} mho . cm^{-1}.

Apparatus and Procedure. The ultraviolet absorption spectra were measured for 2,2'-bipyridyl in acetonitrile with varying amounts of silicon, germanium or tin compound using a Hitachi EPU-2A spectrophotometer with 1 cm quartz cells at 25°±1°C. From the results, the stability constants of the 2,2'-bipyridyl complexes were determined as previously described.[9,10] The electric conductance was measured for acetonitrile solutions containing a definite amount of silicon, germanium or tin compound and varying amounts of 2,2'-bipyridyl, using a Yokogawa F-255A Universal Bridge at 25°±0.5°C.

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Results and Discussion

Composition of the complexes. Figure 1 shows the uv spectra of 2,2'-bipyridyl with varying amounts of $(CH_3)_3SiCl$ in acetonitrile. Plots of the absorbances at 304 and 316 mμ to the mole ratios of $(CH_3)_3SiCl$/Bipy (Figure 2) indicate the formation of the 1:1 complex. Similarly, $(CH_3)_3GeCl$ and $(CH_3)_2SnBr_2$ form the 1:1 complexes with 2,2'-bipyridyl in solution.

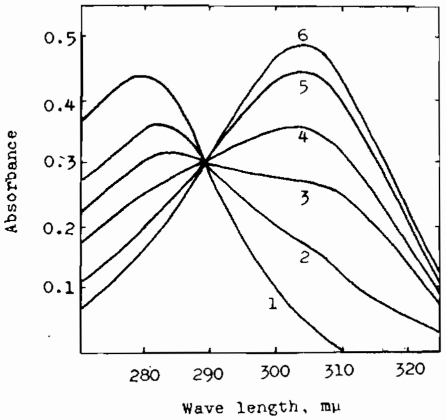

Figure 1. The absorption spectra of 2,2'-bipyridyl (3.00×10^{-5} *M*) in acetonitrile, with varying amounts of $(CH_3)_3SiCl$: (1) 0, (2) 8.88×10^{-6}, (3) 1.48×10^{-5}, (4) 2.07×10^{-5}, (5) 2.96×10^{-5}, (6) 4.44×10^{-5} *M*.

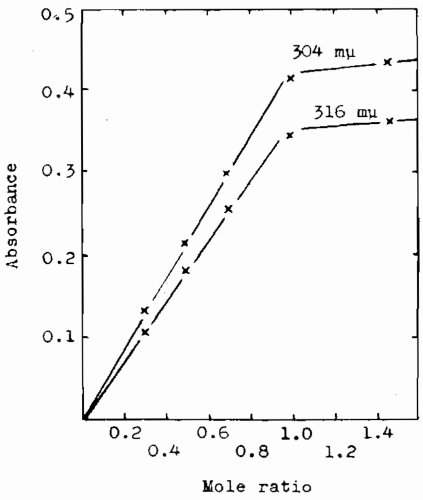

Figure 2. Plots of the absorbance to the mole ratios of $(CH_3)_3SiCl$/Bipy; Bipy, 3.00×10^{-5} *M*.

For the $(CH_3)_2SiCl_2$-Biby system the mole ratio method in the uv spectrum (Figure 3) indicates the formation of the 1:2 complex in acetonitrile. On the other hand, the uv spectra of 2,2'-bipyridyl with varying amounts of $SiCl_4$ in acetonitrile (Figure 4) showed an almost maximum absorbance at 303 mμ when the mole ratio is about 1:0.33, and the absorbance increases only slightly by further additions of $SiCl_4$. The method of continuous variation in the uv spectrum (Figure 5) clearly indicates that $SiCl_4$ forms the 1:3 complex with 2,2'-bipyridyl in acetonitrile.

Similarly, $GeCl_4$ forms the 1:3 complex with 2,2'-bipyridyl in acetonitrile, although 1:1 adducts of $SiCl_4$[2,11] and $GeCl_4$[3,12] with 2,2'-bipyridyl were isolated.

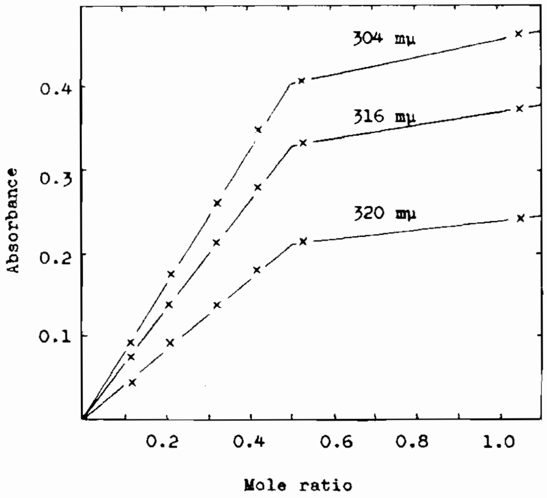

Figure 3. Plots of the absorbance to the mole ratios of $(CH_3)_2SiCl_2$/Bipy; Bipy, 2.94×10^{-5} *M*.

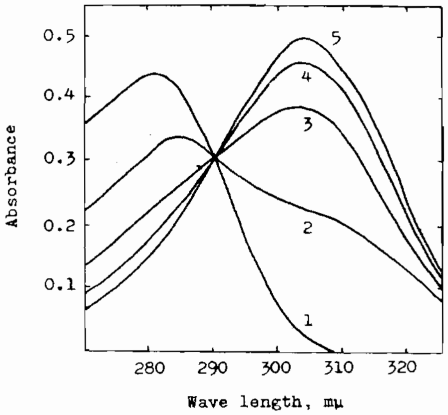

Figure 4. The absorption spectra of 2,2'bipyridyl(3.00×10^{-5} *M*) in acetonitrile with varying amounts of $SnCl_4$: (1) 0, (2) 3.14×10^{-6}, (3) 6.28×10^{-6}, (4) 1.02×10^{-5}, (5) 3.41×10^{-5} *M*.

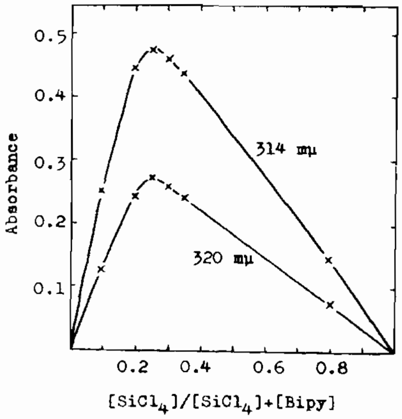

Figure 5. Plots of the absorbance to the ratios of $[SiCl_4]$/$[SiCl_4]+[Bipy]$; $[SiCl_4]+[Bipy]$, 5.23×10^{-5} *M*.

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In the spectra of $(CH_3)_2GeCl_2$- and $(CH_3)_2SnI_2$-Bipy systems in acetonitrile, the absorption bands at 303 mμ also increased in intensity with increasing amount of the germanium or tin compound. However, the composition of the complexes in solution could not be determined either from the mole ratio method or the continuous variation method; these methods showed fairly ambiguous variation between the compositions of 1:1 and 1:2. This may be suggestive of the existence of two or more species for these complexes in solution.

Chemical species of the complexes. The molar conductances obtained are listed in Table I.

Table I. Molar conductances (Λ) of some $(CH_3)_nMX_{4-n}$ (M = Si, Ge, Sn; X = Cl, Br, I; n = 3, 2 or 0) in acetonitrile with varying amounts of 2,2′-bipyridyl at 25°C, mho . cm². mole⁻¹.

$(CH_3)_nMX_{4-n}$	Concentration, $M\times10^3$	Mole ratios, $\frac{[\mathrm{Bipy}]}{[(CH_3)_nMX_{4-n}]}$	Λ [a]
$(CH_3)_3SiCl$	0.79	1	74
	1.96	1	59
	1.96	10	60
$(CH_3)_2SiCl_2$	0.79	2	124
	1.98	2	81
	1.98	20	83
$(CH_3)_3GeCl$	0.91	0	1.3
	0.91	1	2.7
	0.91	30	5.9
$(CH_3)_2GeCl_2$	0.96	0	0.8
	0.96	2	25
	0.96	20	50
$(CH_3)_2SnBr_2$	1.05	0	0.8
	1.05	1	5.4
	1.05	30	6.5
$(CH_3)_2SnI_2$	1.05	0	1.2
	1.04	2	37
	1.01	20	52

[a] Λ of 2.2′-bipyridyl (1.0×10^{-3} *M*) in acetonitrile, 0.053 mho . cm² . mole⁻¹.

Methylsilyl chlorides, methylgermyl chlorides and methyltin halides as well as 2,2′-bipyridyl gave independently non-conducting acetonitrile solutions. It is therefore no doubt that considerably large conductances observed in some cases of silyl, germyl or tin compounds do not result from hydrolysis product of the organometal halides. As is seen in Table I, a solution of equimolar mixture of $(CH_3)_3SiCl$ and 2,2′-bipyridyl and the 1:2 mixture of $(CH_3)_2SiCl_2$ and 2,2′-bipyridyl did not show any appreciable increase in conductance by adding a large excess of 2,2′-bipyridyl. These observations indicate that the complexes of methylsilyl chlorides are little dissociated into the parent molecules in solution. The value for the equimolar mixture of $(CH_3)_3SiCl$ and 2,2′-bipyridyl is an evidence of ionic dissociation as $[(CH_3)_3Si\cdot \mathrm{Bipy}]^+$ and Cl^- in acetonitrile. These species may be compared with $[(C_6H_5)_3Si\cdot \mathrm{Bipy}]^+$ and I^- or Br^- in dichloromethane.[1] The value for the 1:2 mixture of $(CH_3)_2SiCl_2$ and 2,2′-bipyridyl is about one and a half times as large as that for the 1:1 $(CH_3)_3SiCl$-Bipy mixture, suggesting an uni-bivalent electrolyte, $[(CH_3)_2Si\cdot 2\mathrm{Bipy}]^{2+}$ and $2Cl^-$, for the 1:2 complex.

Because of extremely poor solubility of the mixture of MCl_4 (M = Si and Ge) and 2,2′-bipyridyl in acetonitrile, any reliable conductivity measurement for the solutions has not been made. However, these solutions showed an absorption band at 303 mμ, which is associated with the *cis*-configuration of 2,2′-bipyridyl;[13] the both nitrogen atoms coordinate to the silicon or germanium atom. It is unlikely to expect 8- or 10-coordinated structure for $MCl_4\cdot 3\mathrm{Bipy}$ (M = Si or Ge). Chemically the formulation of the species as $[M\cdot 3\mathrm{Bipy}]^{4+}$ and $4Cl^-$ would be satisfactory in dilute solution. The $[Si\cdot 3\mathrm{Bipy}]^{4+}$ cation may be isostructural with tris(2,2′-bipyridyl) silicon(O) isolated previously.[14]

The mixture of $(CH_3)_3GeCl$ or $(CH_3)_2SnBr_2$ and 2,2′-bipyridyl yielded non-conducting acetonitrile solution even when a large excess of the latter was dissolved. This result would confirm to be non-ionic in solution for the complexes $(CH_3)_3GeCl\cdot \mathrm{Bipy}$ and $(CH_3)_2SnBr_2\cdot \mathrm{Bipy}$, in which germanium and tin atoms are hexa-coordinated. On the other hand, the 1:2 mixture of $(CH_3)_2GeCl_2$ or $(CH_3)_2SnI_2$ and 2,2′-bipyridyl in acetonitrile gave somewhat large conductance (Table I), and the values increased considerably by further addition of 2,2′-bipyridyl to the solution. These results may be explained by assuming the following equilibria in solution:

$$\begin{tikzcd}
(CH_3)_2MX_2+2\mathrm{Bipy} \arrow[r, shift left] \arrow[dr, shift left] & (CH_3)_2MX_2\cdot \mathrm{Bipy}+\mathrm{Bipy} \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left] & {[(CH_3)_2M\cdot 2\mathrm{Bipy}]^{2+}+2X^-} \arrow[l, shift left] \arrow[dl, shift left] \\
 & {[(CH_3)_2MX\cdot \mathrm{Bipy}]^{+}+X^-+\mathrm{Bipy}} \arrow[ul, shift left] \arrow[u, shift left] \arrow[ur, shift left] &
\end{tikzcd}$$

where M = Ge and X = Cl, or M = Sn and X = I.

Stability constants. The stability constants of some 2,2′-bipyridyl complexes of silicon, germanium and tin compounds are presented in Table II. For the $(CH_3)_2GeCl_2$-Bipy and $(CH_3)_2SnI_2$-Bipy complexes, the values were calculated from their spectra in the presence of large excesses of the metal compounds (mole ratios of 4:1 to 100:1), under the assumption that the metal compounds form mainly 1:1 adducts with 2,2′-bipyridyl. The stability constants of the $(CH_3)_2SiCl_2$,

Table II. The stability constants, K, of some $(CH_3)_nMX_{4-n}\cdot$ Bipy complexes (M = Si, Ge and Sn; X = Cl, Br or I; n = 3,2 or 0) in acetonitrile.

$(CH_3)_nMX_{4-n}$	Log. K
$(CH_3)_3SiCl$	6.0 ±0.3
$(CH_3)_3GeCl$	3.18±0.02
$(CH_3)_2GeCl_2$	4.38±0.06
$(CH_3)_3SnCl$	1.19±0.02
$(CH_3)_2SnCl_2$	3.30±0.04 [a]
$(CH_3)_2SnBr_2$	3.60±0.01
$(CH_3)_2SnI_2$	4.11±0.09
$SnCl_4$	>7 [a]

[a] Ref. 10.

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[14] R. Pant and H. C. Agrawal, *Naturwissenschaft.*, 50, 330 (1963).

$SiCl_4$ and $GeCl_4$ complexes were too large to be determined accurately by the present spectrophotometric method.

It has previously been pointed out that the strong acceptor power of $SnCl_4$ decreases appreciably by alkyl substitution to the chlorine atom.[9,10] This may also be true for $SiCl_4$ and $GeCl_4$, as is seen in Table II. On the other hand, the stability constants of the $(CH_3)_2SnX_2$ complexes increase in the order of $X = Cl < Br < I$. This is interpreted by assuming that tin-halogen bonds may be more polarized in this order in polar solvents, such as acetonitrile, leading to an increase of acceptor power of tin atom.

The present study does not reveal the relative strength of Lewis acidity of $SiCl_4$, $GeCl_4$ and $SnCl_4$. However, Table II indicates that the order of acceptor property of $(CH_3)_2MCl_2$ or $(CH_3)_3MCl$ toward 2,2'-bipyridyl in acetonitrile is $Si > Ge > Sn$.