

no bands in this area. Furthermore, other work in our laboratory shows that spectra of even monomeric hydroxy species (of As(III)) do not have bands in this region. The  $\sim 1620\text{-cm}^{-1}$  peak may be ascribed in part to the  $\nu_2$  bending mode of water for the following reason. As  $[\text{Bi(III)}]$  increases ( $[\text{Bi(III)}] + [\text{NO}_3^-] = 2.45\text{ M}$ ), this band shifts from  $1640\text{ cm}^{-1}$  ( $R = 7.0$ ) to  $1618\text{ cm}^{-1}$  ( $R = 1.5$ ) and considerably narrows in width. Cations are expected to influence mainly the bending mode of water, and the spectral behavior which we observe has been predicted and found elsewhere for other ions.<sup>24</sup> In addition, there is probably some contribution to the  $1620\text{-cm}^{-1}$  band from the Raman- and infrared-allowed overtone of the  $B_1$  mode of bound  $\text{NO}_3^-$ , as well as from the Raman-allowed overtone of the  $A_2''$  mode of free  $\text{NO}_3^-$ .

An interesting finding of the present study is that water is coordinated to Bi(III) in all of the aqueous

(24) E. R. Nightingale, Jr., in "Chemical Physics of Ionic Solutions," B. E. Conway and R. G. Barradas, Ed., John Wiley and Sons, Inc., New York, N. Y., 1966, p 87.

nitrate complexes. This conclusion follows from the continued presence in all solutions of the symmetric bismuth(III)-water stretching mode at  $\sim 370\text{ cm}^{-1}$  and is not wholly unexpected, since in solid  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  each Bi(III) is capable of coordinating three bidentate nitrates and three water molecules.<sup>6</sup> Moreover, the facts that the normalized molar intensity of this band remains almost constant in all solutions (even though the number of coordinated  $\text{H}_2\text{O}$  molecules is expected to decrease as  $\text{NO}_3^-$  is coordinated) and that its frequency increases with  $R$  suggest that the water in the higher complexes is even more strongly bound than in the lower species. However, in the hydrate melt, which might be considered the most concentrated solution of all, the fact that the Bi- $\text{H}_2\text{O}$  line is not observed indicates that the water has been removed, with a stronger coordination of nitrate. Accompanying this stronger nitrate coordination, the Bi- $\text{NO}_3^-$  frequency increases from  $232\text{ cm}^{-1}$  in the concentrated aqueous solution to  $239\text{ cm}^{-1}$  in the melt.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE MATERIALS RESEARCH CENTER, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201

## Adducts of Group IV Tetrahalides and $\beta$ -Diketones

BY A. L. ALLRED AND DAVID W. THOMPSON

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$\beta$ -Diketones form adducts, without enolization, when combined with various metal halides in inert solvents at low temperatures. Analytical, nuclear magnetic resonance, and infrared data are consistent with the following new complexes being simple 1:1, nonionic adducts having carbonyl groups coordinated to *cis* positions:  $\text{SnCl}_4 \cdot \text{C}_7\text{H}_{12}\text{O}_2$  (prepared from 3,3-dimethylacetylacetone),  $\text{TiCl}_4 \cdot \text{C}_7\text{H}_{12}\text{O}_2$ ,  $\text{TiBr}_4 \cdot \text{C}_7\text{H}_{12}\text{O}_2$ ,  $\text{TiI}_4 \cdot \text{C}_7\text{H}_{12}\text{O}_2$ ,  $\text{ZrCl}_4 \cdot \text{C}_7\text{H}_{12}\text{O}_2$ , and  $\text{SnCl}_4 \cdot \text{C}_6\text{H}_{10}\text{O}_2$  (prepared from 3-methylacetylacetone). The product from the low-temperature reaction of acetylacetone and tin tetrachloride is shown to be the adduct  $\text{SnCl}_4 \cdot \text{C}_5\text{H}_8\text{O}_2$ .

### Introduction

The purpose of the present work was to prepare and investigate adducts in which  $\beta$ -diketones, without enolization, form chelated structures with metal halides.

3,3-Dimethylacetylacetone, (3,3-AcAc), does not contain readily enolizable hydrogens and therefore was selected as a ligand for the observation of reactivity and of infrared and nmr spectra of  $\beta$ -diketone adducts<sup>1</sup> in this investigation. The previously reported diketone adducts of acetylacetone (AcAcH) and its derivatives were characterized only by elemental analyses and decomposition temperatures except where noted:  $\text{BF}_3 \cdot \text{C}_6\text{H}_5\text{COAc}$ ,<sup>2</sup>  $\text{Al}_2\text{Br}_6 \cdot 2\text{AcAcH}$ ,<sup>3</sup> "[ $(\text{HAcAc})_2\text{Sn}$ ] $\text{SnCl}_6$ " (conductivity),<sup>4</sup> "[ $(\text{HAcAc})_2\text{SnCl}_2$ ] $\text{Cl}_2$ " (conductiv-

ity),<sup>4</sup>  $\text{SbCl}_5 \cdot \text{AcAcH}$ ,<sup>5</sup>  $\text{HgCl}_2 \cdot \text{AcAcH}$ <sup>6</sup> (infrared<sup>7</sup>),  $\text{TiCl}_4 \cdot \text{AcAcH}$ ,<sup>5</sup> and  $\text{ZrCl}_4 \cdot \text{AcAcH}$ .<sup>8</sup> Recently,<sup>9</sup> the "very weak complexes"  $\text{SiF}_4 \cdot \text{HAcAc}$  and  $\text{GeF}_4 \cdot \text{HAcAc}$  and the complex  $\text{SnF}_4 \cdot \text{HAcAc}$  were listed in an nmr investigation but apparently were not isolated and analyzed.

Far more common than adducts of  $\beta$ -diketones are the  $\beta$ -ketoenolate complexes. Of interest in the present investigation are conditions in which reaction 1 is favored over reaction 2. As indicated by the following paragraphs, the reaction of tin tetrachloride and acetylacetone is reported<sup>4,5,10-12</sup> to give at least one ill-defined product in addition to *cis*-dichlorobis(acetylacetonato)-tin(IV).

(1) The term "adduct" herein refers to Lewis acid-base compounds not having enolate ligands.

(2) H. Meerwein and D. Vossen, *J. Prakt. Chem.*, **141**, 149 (1934).

(3) E. P. Kohler, *Am. Chem. J.*, **27**, 241 (1902).

(4) R. C. Mehrotra and V. D. Gupta, *J. Indian Chem. Soc.*, **40**, 911 (1963).

(5) A. Rosenheim, W. Loewenstamm, and L. Singer, *Ber.*, **36**, 1833 (1903).

(6) G. B. Marini-Bettolo and L. Paoloni, *Gazz. Chim. Ital.*, **75**, 78 (1945).

(7) L. Paoloni, *ibid.*, **89**, 2171 (1959).

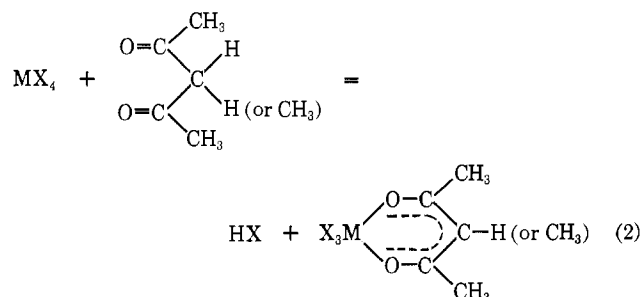
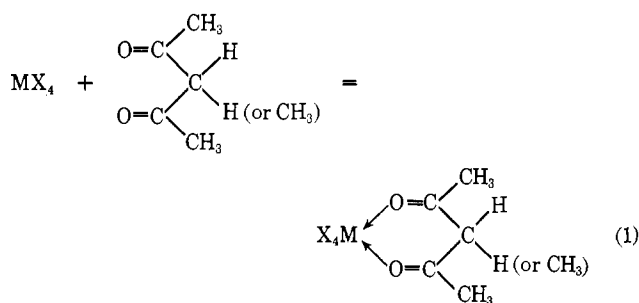
(8) G. Jantsch, *J. Prakt. Chem.*, **115**, 7 (1927).

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

(10) W. Dilthey, *Ber.*, **36**, 923 (1903).

(11) W. Dilthey, *Ann. Chem.*, **344**, 300 (1906).

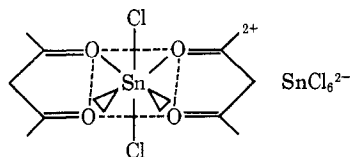
(12) G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 372 (1924).



The reaction between tin tetrachloride and acetylacetone in refluxing benzene was studied initially in 1903 by Dilthey<sup>10,11</sup> and Rosenheim, *et al.*,<sup>5</sup> who isolated a product having the empirical formula  $\text{SnCl}_2 \cdot (\text{C}_5\text{H}_7\text{O}_2)_2$ . On the basis of the high melting point, 202–204°, Dilthey suggested a structure involving tris(acetylacetonato)tin(IV) and hexachlorostannate(IV) ions. In 1924 Morgan and Drew<sup>12</sup> obtained the same product and from molecular weight data concluded that it was “monomeric stannic bisacetylacetonate dichloride.”

Morgan and Drew also found<sup>12</sup> that the reaction of acetylacetone and tin tetrachloride at room temperature gave a product different from that isolated after refluxing in benzene. This new product, mp 150°, was assumed to be an equimolar mixture of the “stannic bisacetylacetonate dichloride” and hexachlorostannic acid.

In 1963 the tin tetrachloride–acetylacetonate system was investigated by Mehrotra and Gupta,<sup>4</sup> who established that the product of the reaction in refluxing benzene and chloroform is the monomeric, hexacoordinate dichlorobis(acetylacetonato)tin(IV) complex. The *cis* structure was assigned later.<sup>13–16</sup> Mehrotra and Gupta also attempted to elucidate the above “mixture” formed by the reaction at room temperature. Their analytical data confirmed the empirical formula  $\text{SnCl}_4 \cdot \text{C}_5\text{H}_8\text{O}_2$ . An “intermediate” having the formula  $[(\text{HAcAc})_2\text{SnCl}_2]\text{Cl}_2$  was also claimed. Because the solid was unchanged under vacuum ( $10^{-4}$  mm) at 55°, they ruled out the possibility of hexachlorostannic acid which melts at 51°. On the basis of conductance data and chemical evidence, they drew the conclusion that the diketone complex should be formulated as



This structure will be mentioned again after a discussion of experiments involving the addition of acetylacetone, 3-methylacetylacetonate, and 3,3-dimethylacetylacetonate to some group IVa and IVb halides.

### Experimental Section

**Reagents.**—The following chemicals were purchased: titanium tetrafluoride, titanium tetrabromide, titanium tetraiodide, and zirconium tetrafluoride (Alfa Inorganics, Inc.); tin and titanium tetrachlorides, “purified” grade (City Chemical Corp.); zirconium tetrachloride, “hafnium-free, reactor grade” (City Chemical Corp.); tin tetrafluoride (Peninsular Chemresearch, Inc.); germanium tetrachloride (Bagle Pitcher, Inc.); silicon tetrachloride (Fischer Scientific Co., Inc.). The tetrafluorides of silicon and germanium were gifts from Dr. D. F. Shriver. Tin tetraiodide and tin tetrabromide were prepared according to a published procedure.<sup>17</sup> Tin tetrachloride, titanium tetrachloride, and titanium tetrabromide were distilled under nitrogen before use. Other compounds, except where noted in the subsequent experimental details, were used without further purification. Acetylacetone was obtained from Eastman Organic Chemicals and was distilled before use. All solvents were purified by distillation from suitable dehydrating agents before use. Methylene chloride with <0.01% water (Matheson Coleman and Bell) was refluxed over and distilled from calcium hydride under nitrogen.

**General Procedures.**—Except when otherwise noted, the following general procedures apply in reactions of the metal halides. All attempted preparations were carried out under an atmosphere of dry nitrogen in small round-bottom flasks equipped with a dropping funnel, a magnetic stirrer, and a nitrogen inlet. Before any materials were added, the apparatus was thoroughly flamed under a dry nitrogen stream. All liquid components were transferred with syringes. Resulting solids were transferred under nitrogen to a Schlenk-type filtration apparatus.<sup>18</sup> After the compounds were washed with the solvent, they were dried under high vacuum at room temperature.

**3-Methylacetylacetonate** was prepared according to the procedure in ref 19. However, in order to reduce the possibility of forming 3,3-dimethylacetylacetonate, only one-third of the recommended amount of methyl iodide was used. The final product was purified by fractional distillation. Nmr and gas chromatographic data as well as elemental analysis indicated that the compound was pure; bp 172° (745 mm).

*Anal.* Calcd for  $\text{C}_6\text{H}_{10}\text{O}_2$ : C, 63.13; H, 8.83. Found: C, 63.03; H, 8.88.

**3,3-Dimethylacetylacetonate** was prepared in nearly the same manner as described previously<sup>19</sup> for 3-methylacetylacetonate. The crude product from the 3-methylacetylacetonate preparation was used in place of acetylacetonate. A large excess of methyl iodide (approximately twofold) was used in order to obtain complete methylation of the 3-methylacetylacetonate. The product was separated by fractional distillation and gas chromatographic and analytical data indicated that it was pure; bp 174° (745 mm);  $n_{\text{D}}^{20}$  1.4272, lit.<sup>20</sup>  $n_{\text{D}}^{27}$  1.426; yield ~80%.

*Anal.* Calcd for  $\text{C}_7\text{H}_{12}\text{O}_2$ : C, 65.60; H, 9.44. Found: C, 65.41; H, 9.34.

**Reactions of 3,3-Dimethylacetylacetonate with Tin Tetrachloride, Titanium Tetrachloride, Titanium Tetrabromide, Titanium Tetraiodide, and Zirconium Tetrachloride.**—In a typical reaction, tin tetrachloride (13.3 g,  $5.1 \times 10^{-2}$  mol) was added to 20 ml of methylene chloride, and the resulting solution was cooled to 0°. Then 3,3-dimethylacetylacetonate (6.7 g,  $5.2 \times 10^{-2}$  mol) in 10 ml of methylene chloride was added dropwise, after which

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(20) K. V. Auwers, *Ann. Chem.*, **415**, 224 (1918).

TABLE I  
 β-DIKETONE ADDUCTS AND ANALYTICAL DATA

	Color	Mp, °C	Analyses, %					
			Calcd			Found		
			C	H	X	C	H	X
SnCl <sub>4</sub> (C <sub>7</sub> H <sub>12</sub> O <sub>2</sub> )	White	90-93	21.63	3.11	36.49	21.49	3.13	36.24
TiCl <sub>4</sub> (C <sub>7</sub> H <sub>12</sub> O <sub>2</sub> )	Yellow	126-128	26.45	3.81	44.61	26.60	3.90	44.52
TiBr <sub>4</sub> (C <sub>7</sub> H <sub>12</sub> O <sub>2</sub> )	Red	129-130	16.96	2.44	64.48	16.81	2.41	64.41
TiI <sub>4</sub> (C <sub>7</sub> H <sub>12</sub> O <sub>2</sub> )	Purple	111-115	12.30	1.77	74.25	12.26	1.88	71.43
ZrCl <sub>4</sub> (C <sub>7</sub> H <sub>12</sub> O <sub>2</sub> )	Gray-white	163-166	23.27	3.35	39.26	23.52	3.68	...
SnCl <sub>4</sub> (C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> )	White	...	16.65	2.23	39.33	16.78	2.37	39.17
SnCl <sub>4</sub> (C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> )	White	128-131	19.23	2.69	37.85	20.53	2.87	37.36
TiCl <sub>4</sub> (C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> )	Red-orange	174-185	20.72	2.78	48.92	20.51	2.45	38.96

only a small amount of solid was evident. *n*-Hexane (20 ml) was added dropwise to the mixture whereupon additional white solid formed. This solid was filtered off, washed with *n*-hexane, and dried. For some of these reactions, sufficient precipitation occurred without the addition of hexane. Carbon disulfide was the solvent for the reaction of 3,3-dimethylacetylacetone with titanium tetraiodide.

**Attempted Preparation of Other Lewis Acid-3,3-Dimethylacetylacetone Adducts.**—In procedures similar to those described above, tin tetrabromide, tin tetraiodide, germanium tetrachloride, silicon tetrachloride, and zirconium tetrafluoride were combined with 3,3-dimethylacetylacetone. In all cases the starting materials were recovered. A tensiometric study with silicon tetrafluoride gave no evidence for adduct formation at 25°.

The reaction of titanium tetrafluoride and germanium tetrafluoride with 3,3-dimethylacetylacetone in various solvents appeared to give adducts. However, only intractable materials could be obtained. These were not analyzed further.

When tin tetrafluoride is stirred with 3,3-dimethylacetylacetone in an inert solvent, the mixture gradually becomes brown. At reflux temperature the mixture rapidly turns brown. No solid adduct could be isolated.

**Reaction of Tin Tetrachloride with Acetylacetone at 0°.**—Methylene chloride (15 ml) and tin tetrachloride (8.9 g, 3.4 × 10<sup>-2</sup> mol) were placed in the reaction vessel and the resulting solution was thermally equilibrated in an ice bath. Upon the slow addition of acetylacetone (3.9 g, 3.9 × 10<sup>-2</sup> mol) in methylene chloride (10 ml), a white precipitate began to form immediately and the colorless solution gradually became yellow. The white solid was isolated and with heating it appeared to decompose: at 135° liquid was noticed on the capillary walls, at 165° the remaining solid began to darken, and at 169-175° vigorous melting led to a clear brown liquid (lit.<sup>4</sup> mp 151°).

The filtrate from the above reaction was yellow. Removal of the solvent at room temperature, without exposing the solution to the air, gave only an orange oil. An infrared spectrum of this oil showed it to consist of free acetylacetone, possibly the adduct between tin tetrachloride and acetylacetone, and a chelated acetylacetonate complex. Crystals were obtained from this oil by dissolution in ethyl acetate followed by addition of *n*-hexane to the point of cloudiness. After being heated a few minutes on a steam bath, this solution was filtered in the air through charcoal. Slow cooling in a refrigerator gave off-white crystals. The infrared and nmr spectra as well as melting point (202-204°) were identical with that for the dichlorobis(acetylacetonato)tin(IV) complex.

The above reaction was carried out in benzene, chloroform, and carbon tetrachloride. In all cases the infrared spectrum showed the products to be identical, with the best-appearing compounds being obtained in methylene chloride and chloroform.

**Reaction of Titanium Tetrachloride with Acetylacetone at 0°.**—A methylene chloride (20 ml) solution of titanium tetrachloride (6.9 g, 3.6 × 10<sup>-2</sup> mol) was thermally equilibrated in an ice bath. Dropwise addition of acetylacetone (3.9 g, 3.9 × 10<sup>-2</sup> mol) in 10 ml of methylene chloride gave an immediate yellow precipitate. After filtration and washing with methylene chloride, a yellow solid remained which turned red-orange on vacuum drying.

**Reactions of Silicon Tetrachloride, Germanium Tetrachloride, and Zirconium Tetrachloride with Acetylacetone at 0°.**—These tetrachlorides were allowed to react with acetylacetone in 1:1 molar ratios. Silicon tetrachloride and germanium tetrachloride gave no evidence of reacting with acetylacetone at 0° to give either an adduct or enolate complex. Zirconium tetrachloride, however, gives only an enolate complex at 0° for which analytical data were consistent with the reported<sup>18</sup> dichlorobis(acetylacetonato)zirconium(IV).

**Reaction of Tin Tetrachloride and 3-Methylacetylacetone at 0°.**—To tin tetrachloride (8.9 g, 3.4 × 10<sup>-2</sup> mol) dissolved in 20 ml of methylene chloride was added 3-methylacetylacetone (4.1 g, 3.6 × 10<sup>-2</sup> mol) in 10 ml of methylene chloride. A white precipitate formed immediately, and the solution gradually became yellow. The solid product was filtered off, washed with small portions of methylene chloride, and dried.

**Reaction of the Tin Tetrachloride-Acetylacetone Adduct with Water.**—A mixture of the acetylacetone adduct of tin tetrachloride in an excess of water was stirred for a few minutes, and the remaining solid was filtered, washed with ether, and recrystallized from ethyl acetate; mp 203-205°. The nmr and infrared spectra showed the compound to be identical with the reported *cis*-dichlorobis(acetylacetonato)tin(IV).<sup>14,16</sup>

**Reaction of *cis*-Dichlorobis(acetylacetonato)tin(IV) with Hydrogen Chloride.**—Gaseous hydrogen chloride was passed through a stirred solution of *cis*-dichlorobis(acetylacetonato)tin(IV) (1.0 g) in 25 ml of methylene chloride at 0°. Within a few hours the solid disappeared and a clear oil formed. The reaction mixture was filtered, and to the slightly yellow filtrate was added 10 ml of *n*-hexane. Upon removal of half of the solvent mixture by vacuum distillation, a very viscous oil formed. After the oil was stirred for 1 hr, white crystals formed. The infrared spectrum of this solid was identical (except for weak enolate bands in the 1500-1600-cm<sup>-1</sup> region) with that for the product formed by the reaction of tin tetrachloride and acetylacetone at 0° as described above.

**Analyses.**—The analyses were done by Schwarzkopf Micro-analytical Laboratory. 3-Methylacetylacetone and 3,3-dimethylacetylacetone were analyzed by Micro-Tech Laboratories, Inc. Analytical data for the adducts are listed in Table I.

**Infrared Spectra.**—The infrared spectra reported in Table II were taken with Beckman IR-9, IR-10, and IR-11 spectrophotometers with exact band positions being read from the IR-9 and IR-11 instruments only. Solid-state spectra were run as Nujol mulls. For those compounds sensitive to moisture, mulls as well as solutions were prepared in a glove bag filled with dry nitrogen and containing a dish of P<sub>2</sub>O<sub>5</sub>. For the middle- and far-infrared regions, potassium bromide and polyethylene plates were used, respectively. The following symbols were used to describe the absorption bands: vw, very weak; w, weak; m, medium; s, strong; sh, shoulder; br, broad.

**Nuclear Magnetic Resonance Spectra** were taken with a Varian A-60 spectrometer. The data are contained in Table II.

**Melting Points.**—All melting points were taken in sealed capillaries and are uncorrected. The reported melting points are for the regions of vigorous melting. Many of the compounds appeared to be undergoing some decomposition before melting completely.

TABLE II  
 NUCLEAR MAGNETIC RESONANCE AND INFRARED DATA

	Proton chemical shifts <sup>a</sup>		Temp, °C	$\nu$ , 1500-1800 cm <sup>-1</sup>		$\nu$ , 500-600	$\nu$ , 200-500 cm <sup>-1</sup>
	$\delta_{\text{CH}_3}$ , ppm 1,5 positions	3 position		Mull	In CH <sub>2</sub> Cl <sub>2</sub>	cm <sup>-1</sup> Mull	
3,3-AcAc	2.20	1.38	37		1721 m	596 w	
	2.24	1.40	-18		1703 s	561 w	
	2.23	1.39	-51			509 vw	
SnCl <sub>4</sub> ·3,3-AcAc	2.24	1.40	37	1680 s, br	1722 m	575 s	405 m, 303 m
	2.43	1.51	-18	1607 vw	1703 s		355 s, 247 m
	2.66	1.68	-51		1665 w, br		341 s, 214 m
TiCl <sub>4</sub> ·3,3-AcAc	2.74	1.88	37	1691 s	1707 s	563 s	426 m, 374 s, 220 m
	2.80	1.94	-18	1621 w	1647 w, br		416 m, 312 w
	2.84	1.97	-51				394 s, 267 vw
TiBr <sub>4</sub> ·3,3-AcAc	2.70	1.86	37	1689 s	1704 s	560 m	414 m, 320 s, br, 228 s
	2.79	1.94	-18	1618 w	1640 w, br		376 w, 289 s
	2.80	1.93	-51				330 sh, 245 s
TiI <sub>4</sub> ·3,3-AcAc				1680 s			404 m, 266 vw
	<i>b</i>	...	...	1614 w	<i>b</i>	556 m	310 s, 221 s
							294 s
ZrCl <sub>4</sub> ·3,3-AcAc	2.68	1.78	37	1644 s	1704 s	574 m	440 m, 318 s, 202 sh
	2.71	1.79	-18	1597 m	1655 w, br	531 m	431 m, 275 sh
	2.73	1.81	-51				339 vs, br, 207 m
3-AcAc	...	...	...		1760 w, 1610 m, br	569 w	
					1729 m		
					1708 s		
SnCl <sub>4</sub> ·3-AcAc				1673 s, br	1729 m, 1625 vw	583 m	472 m, 334 s
	...	...	...	1613 w	1703 s, 1570 s	545 m	463 sh, 305 m
					1665 m, 1526 s		396 s, 257 m
							364 s
HAcAc					1731 m	531 w	
	2.30 <sup>c</sup>	...	-25 to 37		1709 m	513 w	
					1617 s, br		
SnCl <sub>4</sub> ·HAcAc				1731 vw	1735 w, 1597 m		472 vw, 344 vs, 232 s
	2.38	...	37	1670 s, br	1702 m, 1568 s	562 m	452 w, 298 s
					1667 w, br, 1542 s		389 s, 253 m
					1616 vw		
TiCl <sub>4</sub> ·HAcAc				1683 s			488 vw, 376 s, 246 vw
	...	...	...	1633 w		545 s	421 m, 307 w, 231 w
							390 s, 267 vw
SnCl <sub>2</sub> (C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub>	2.20		-25 to 37	1572 sh	1579 m	595 m	461 s, 334 vs, br, 231 s
	2.30	...		1540 s, br	1561 s	558 vw	421 m, 219 w, br
					1542 s		415 m, 266 m

<sup>a</sup> Internal standard, tetramethylsilane; solvent, methylene chloride. <sup>b</sup> Not measured owing to low solubility. <sup>c</sup>  $\delta_{\text{CH}_3} = -2.12$  ppm for the enol tautomer.

## Results and Discussion

### A. Lewis Acid-Base Adducts of $\beta$ -Diketones.—

The solid 1:1 adducts formed upon combination of 3,3-dimethylacetylacetone with various group IV tetrahalides are summarized in Table I. Silicon tetrafluoride, silicon and germanium tetrachlorides, tin tetrabromide, and tin tetraiodide did not appear to form adducts with 3,3-AcAc. Germanium, tin, and titanium tetrafluorides appeared to react with 3,3-AcAc; however, only intractable materials could be isolated. All of the adducts are moisture sensitive, and exposure to the atmosphere effects visible decomposition.

When acetylacetone is added to silicon and germanium tetrachlorides in an inert organic solvent at room temperature, no evidence for adduct formation is obtained. Tin tetrachloride, as discussed in part B below, and titanium tetrachloride do form 1:1 adducts with acetylacetone at 0°, and these adducts are stable at room temperature. At elevated temperatures, tin tetrachloride reacts with acetylacetone to give only

*cis*-dichlorobis(acetylacetonato)titanium(IV) regardless of the molar ratios of the reactants.<sup>4</sup> Titanium tetrachloride, on the other hand, gives trichloroacetylacetonato-titanium(IV) when allowed to react in a 1:1 molar ratio with acetylacetone and *cis*-dichlorobis(acetylacetonato)titanium(IV) when combined in a 1:2 molar ratio with acetylacetone.<sup>21-23</sup> When acetylacetone is allowed to react with zirconium tetrachloride in 1:1 molar ratios at 0° or higher temperatures, hydrogen chloride is given off and only the reported<sup>13</sup> dichlorobis(acetylacetonato)zirconium(IV) is isolated.

Qualitatively, silicon and germanium tetrachlorides have much less of a tendency to form adducts than the tetrachlorides of tin, titanium, and especially zirconium. Also, adduct formation with chlorides is more favorable than with bromides or iodides.

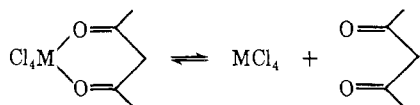
The proton chemical shifts, listed in Table II, of the

(21) D. M. Puri, K. C. Pande, and R. C. Mehrotra, *J. Less-Common Metals*, **4**, 481 (1962).

(22) D. C. Bradley and C. E. Holloway, *Chem. Commun.*, 284 (1965).

(23) R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **6**, 1512 (1967).

adducts of 3,3-dimethylacetylacetone are downfield relative to the free base. Deshielding is due, presumably, to the transfer of electron density from the ligand to the Lewis acid. The dependence on temperature of the two resonance positions observed for each adduct of 3,3-dimethylacetylacetone dissolved in methylene chloride is attributed to partial dissociation and to the ligand jumping rapidly between free and complexed sites. The tin tetrachloride-3,3-dimethyl-



acetylacetone adduct shows the greatest temperature dependence of the adducts studied and at room temperature is almost completely dissociated. Extensive dissociation is also consistent with the much greater apparent solubility of this adduct in methylene chloride in comparison with the other adducts of 3,3-dimethylacetylacetone.

Infrared spectral data for the region of carbonyl stretching, 1500–1800  $\text{cm}^{-1}$ , are tabulated in column 5 of Table II. As expected, the carbonyl stretching frequency is less for the adducts in the solid state than for pure 3,3-dimethylacetylacetone. Since  $\Delta\nu_{\text{C=O}}$  values as great as 145  $\text{cm}^{-1}$  have been observed<sup>24</sup> for monodentate ligands, the carbonyl shifts of the 3,3-dimethylacetylacetone adducts are relatively small. For the tetrachlorides,  $\Delta\nu_{\text{C=O}}$  increases in the order:  $\text{TiCl}_4 < \text{SnCl}_4 < \text{ZrCl}_4$ . For the titanium halides,  $\Delta\nu_{\text{C=O}}$  increases in the order:  $\text{TiCl}_4 \sim \text{TiBr}_4 < \text{TiI}_4$ .

The infrared spectra of the adducts of 3,3-dimethylacetylacetone in methylene chloride (summarized in Table II) differ appreciably from the corresponding solid-state spectra in the carbonyl region. For the tin tetrachloride adduct, bands are observed at 1722, 1703, and 1665  $\text{cm}^{-1}$ ; the bands at 1722 and 1703  $\text{cm}^{-1}$  have the same relative molar absorptivities and frequencies as corresponding bands of free 3,3-dimethylacetylacetone. The small nmr chemical shift in the tin tetrachloride-3,3-dimethylacetylacetone relative to free 3,3-dimethylacetylacetone and the other 3,3-dimethyl adducts studied is in agreement with the solution infrared results.

The infrared absorptions in the 200–500- $\text{cm}^{-1}$  region, Table II, probably contain contributions from both Sn-Cl and Sn-O stretching vibrations. For complexes of the type  $\text{SnCl}_4\text{L}_2$ ,  $\nu_{\text{Sn-Cl}}$  generally occurs in the range 280–400  $\text{cm}^{-1}$ <sup>25–27</sup> and for  $\text{SnCl}_4(\text{ONC}_5\text{H}_5)_2$ ,  $\nu_{\text{Sn-O}}$  is at 382  $\text{cm}^{-1}$ .<sup>27</sup> While detailed assignments of peaks to tin-chlorine and tin-oxygen stretching was not attempted, the total number of peaks is consistent with a *cis* but not a *trans* (polymeric) structure.

The 1:1 adducts with 3,3-AcAc should have a *cis* structure, and a listing of the far-infrared bands should prove useful in deciding between *cis* or *trans* structures

(24) B. Susz, *Compt. Rend.*, **248**, 2559 (1959).

(25) I. R. Beattie, B. P. McQuillan, L. Rule, and M. Webster, *J. Chem. Soc.*, 1514 (1963).

(26) P. Hunt and D. P. N. Satchell, *ibid.*, 5437 (1964).

(27) C. J. Wilkins and H. M. Haendler, *ibid.*, 3174 (1965).

of 1:2 adducts of monodentate donors. The bis-acetone adduct of tin tetrachloride has the possibility of a *cis* or *trans* structure. If *trans*, the adduct has pseudo- $D_{4h}$  symmetry and only one infrared-active Sn-Cl stretch, whereas the *cis* adduct would have  $C_{2v}$  symmetry giving four infrared-active stretches. Beattie and Rule<sup>28</sup> have used far-infrared data in the region 500–270  $\text{cm}^{-1}$  to suggest that the acetone adduct has a *cis* structure. However, they qualify their conclusion by stating: "Ideally, a known chelate, closely related to the relevant unidentate ligand, should be examined to obtain the spectrum of the *cis* adduct." The bis-acetone adduct was prepared again in this investigation, and the observed bands at 427, 356, 332, and 306  $\text{cm}^{-1}$  agreed well with the reported bands.<sup>28</sup> From the close resemblance of the spectra for the bis-acetone and 3,3-AcAc adducts of tin tetrachloride, it seems reasonably certain that the assignment of a *cis* structure to the acetone adduct is correct.

**B. Characterization of the Tin Tetrachloride- $\beta$ -Diketone Systems.**—The 1:1 tin tetrachloride-acetylacetone adduct when exposed to the atmosphere gradually lost hydrogen chloride and, from infrared and nmr spectra, decomposed to an enolate complex.

However, the interaction in refluxing benzene of 3-methylacetylacetone with tin tetrachloride does not lead to a well-defined product. The solid product had a very poor melting point but showed a strong enolate band at 1574  $\text{cm}^{-1}$ . Smith and Wilkins<sup>15</sup> reported an unsuccessful attempt to prepare dichlorobis(3-methylacetylacetonato)tin(IV). No evidence for  $[(\text{HAcAc})_2\text{SnCl}_2]\text{Cl}_2^4$  was obtained in this investigation.

When the 1:1 acetylacetone-tin tetrachloride adduct was stirred in water, a different white solid formed, which was *cis*-dichlorobis(acetylacetonato)tin(IV). This reaction with water is chemical evidence that the 1:1 compound is simply an adduct, since acetylacetone when added to a water-tin tetrachloride solution gives only *cis*-dichlorobis(acetylacetonato)tin(IV) as observed previously<sup>29</sup> and currently in this research. The product from 3-methylacetylacetone and tin tetrachloride gave an oil when dissolved in water; however, after stirring a few minutes, a white solid formed which contained enolate bands in the infrared spectrum. This solid melted over a wide range and was not identified.

Infrared spectroscopy readily allows one to distinguish adduct formation with enolizable  $\beta$ -diketones from the formation of the enolate complex through elimination of hydrogen chloride. Characteristic regions of absorption of enolate complexes are well known.<sup>30,31</sup> The absence of enolate bands in the 1500–1600- $\text{cm}^{-1}$  region in the infrared spectra of the solid compounds establishes that acetylacetone and 3-meth-

(28) I. R. Beattie and L. Rule, *ibid.*, 3267 (1964).

(29) R. Ueeda, Y. Kawasaki, T. Tanaka, and R. Okuwara, *J. Organometal. Chem. (Amsterdam)*, **5**, 194 (1966).

(30) K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066 (1961).

(31) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 216–225.

ylacetylacetonone do not immediately eliminate hydrogen chloride when allowed to react with tin tetrachloride at room temperature or below, and thus the infrared spectra suggest the formation of adducts similar to that formed between the nonenolizable 3,3-AcAc and tin tetrachloride. A moderately intense band was always observed in the region 540–590  $\text{cm}^{-1}$  for the solid adducts studied here. The free ligands and  $\text{SnCl}_2 \cdot (\text{C}_5\text{H}_7\text{O}_2)_2$  either did not absorb or gave weak peaks in this region.

The solid-state and solution infrared spectra of the acetylacetonone–tin tetrachloride system show that the predominating species in the two phases are not the same. For the adduct in methylene chloride, weak bands were observed at 1735 (vw), 1702, 1667, and 1616 (vw)  $\text{cm}^{-1}$  and strong bands at 1597, 1568, and 1542  $\text{cm}^{-1}$ . The highest energy band at 1735  $\text{cm}^{-1}$  is probably due to the free keto tautomer, while the bands at 1702 and 1667  $\text{cm}^{-1}$  may be due to an adduct. The peak at 1616  $\text{cm}^{-1}$  can be attributed to the enol tautomer of acetylacetonone, and the absorption in the 1500–1600- $\text{cm}^{-1}$  region is most probably due to a ketoenolate complex. The latter complex cannot be *cis*-dichlorobis(acetylacetonato)tin(IV) which in solutions of methylene chloride absorbs at 1579  $\text{cm}^{-1}$  and, as observed here and previously,<sup>14,16</sup> exhibits two methyl resonances. Another possible ketoenolate complex is trichloroacetylacetonatotin(IV).

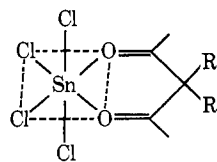
From Table II it is evident that the 3-methylacetylacetonone–tin tetrachloride system is similar to the acetylacetonone system. The band at 1665  $\text{cm}^{-1}$  in the spectrum of the solution is more intense than in the acetylacetonone case. For the 3,3-AcAc·SnCl<sub>4</sub> system, as discussed previously, both free diketone bands and a band at 1665  $\text{cm}^{-1}$  were observed. Within the tin tetrachloride– $\beta$ -diketone systems, 3,3-dimethylacetylacetonone appears to be less basic than 3-methylacetylacetonone which is less basic than acetylacetonone toward tin tetrachloride. With titanium tetrachloride, 3,3-dimethylacetylacetonone again exhibits a smaller carbonyl shift when compared to acetylacetonone. If the differences in the magnitudes of the carbonyl perturbations in acetylacetonone and the 3-methyl-substituted acetylacetonone on coordination to tin and titanium tetrachloride are mainly determined by the electronic differences brought about by substitution at the 3 position, then the methyl group at the 3-carbon can be considered to be electron withdrawing relative to hydrogen. This electron withdrawal should decrease the basicity of the carbonyl oxygens. Laurie and Muentner<sup>32</sup> have recently shown that the methyl group is electron with-

drawing relative to hydrogen in saturated hydrocarbons.

The similarity among the far-infrared spectra, Table II, of the solid 1:1 compounds of tin tetrachloride with acetylacetonone, 3-methylacetylacetonone, and 3,3-dimethylacetylacetonone is further evidence that these compounds are isostructural adducts. The lack of an absorption near 318  $\text{cm}^{-1}$ , which is the absorption region for the hexachlorostannate ion,<sup>33</sup> makes it unlikely that the compounds have the structure postulated by other workers<sup>4</sup> and mentioned in the Introduction. Rather, the data seem most consistent with the above-mentioned compounds being 1:1 adducts.

In the nmr spectrum of the product isolated from the reaction of tin tetrachloride and acetylacetonone and dissolved in dilute solutions ( $\sim 0.1 M$ ) of methylene chloride, only one methyl resonance peak could be observed in the temperature range  $-25$  to  $37^\circ$ . The position of the resonance, the absence of a  $-\text{CH}_2-$  resonance, and the presence in the infrared spectrum of intense bands in the ketoenolate complex region are consistent with assigning the resonance peak to the terminal methyl groups of a ketoenolate complex.

In summary, acetylacetonone, 3-methylacetylacetonone, and 3,3-dimethylacetylacetonone, when allowed to react with tin tetrachloride at  $0^\circ$ , do not eliminate hydrogen chloride but form relatively stable adducts of 1:1 stoichiometry. All observations are consistent with the solid adducts having the structure (where  $R_1 = \text{H}$  or  $\text{CH}_3$ )



although a dimeric structure with bridging  $\beta$ -diketone groups cannot be excluded. Infrared and nmr spectroscopic data indicate that the adducts partially dissociate in methylene chloride and, if enolization is possible, lose some hydrogen chloride to form enolate complexes. The equilibrium of the enolate and the adduct of acetylacetonone can be shifted toward the adduct by the addition of hydrogen chloride.

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(33) N. N. Greenwood and B. P. Straughan, *J. Chem. Soc., A*, 962 (1966).