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Preparation and Characterization of Diiodobis(acetylacetonato)titanium(IV)

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Diiodobis(acetylacetonato)titanium(IV), $Ti(acac)_2I_2$, has been prepared by reaction of acetylacetone with titanium(IV) iodide in diethyl ether solution. The compound is unstable with respect to hydrolysis and oxidation to I_3^-. Conductance, esr, and low-temperature nmr studies indicate that $Ti(acac)_2I_2$ exists in dichloromethane solution as ~50% *cis*-$Ti(acac)_2I_2$, ~40% *trans*-$Ti(acac)_2I_2$, ~10% of an electrolytic dissociation product, presumably $[Ti(acac)_2I]^+I^-$, and 0.13% of a paramagnetic Ti(III) species. The nmr spectra exhibit the effects of rapid *cis–trans* isomerization, exchange of methyl groups between the nonequivalent sites of the *cis* isomer, and exchange of acetylacetonate ligands between the Ti(III) and Ti(IV) environments.

Introduction

Previous papers from this laboratory have described the preparation and properties of dihalobis(acetylacetonato)titanium(IV) complexes, $Ti(acac)_2X_2$, where X = F, Cl, or Br.[1-3] These compounds are only very slightly dissociated in ionizing solvents, and they exist in solution as nonrigid *cis* geometrical isomers.[1-5] The corresponding zirconium and hafnium compounds[6,7] and the complexes which titanium forms with other β-dicarbonyl ligands[8,9] behave similarly.

No diiodobis-β-diketonato complexes have been reported for any of the metals of the titanium subgroup. Until recently, our attempts to prepare the titanium compounds have afforded only intractable oils and solids of nonreproducible composition. We now report the synthesis and characterization of the unstable complex, $Ti(acac)_2I_2$. This compound has proved to be of considerable interest because its behavior is in a number of respects strikingly different from that of the difluoro, dichloro, and dibromo analogs.

Experimental Section

Reagents and General Techniques.—Acetylacetone (Matheson Coleman and Bell, bp 136–140°) was used as purchased without further purification. Anhydrous titanium(IV) iodide was prepared by reaction of the elements,[10] and $Ti(acac)_2Cl_2$ and $[Si(acac)_3]Br$ were synthesized as described previously.[2,11]

Solvents were dried by refluxing for at least 12 hr over an appropriate drying agent. Diethyl ether, tetrahydrofuran, benzene, and hexane were refluxed over lithium aluminum hydride; dichloromethane and carbon tetrachloride were dried over calcium hydride. Nitrogen and oxygen were dried by passing the gases through a 50 × 4.5 cm tower containing Aquasorb.

All operations involved in the synthesis and subsequent handling of compounds were conducted under dry nitrogen or argon. It is emphasized that $Ti(acac)_2I_2$ is very sensitive to atmospheric oxygen and water vapor, and special care must be taken to avoid oxidation and hydrolysis, particularly when working with solutions.

Diiodobis(2,4-pentanedionato)titanium(IV).—A mixture of freshly sublimed titanium(IV) iodide (*ca.* 5 g) and 300 ml of diethyl ether was allowed to reflux for *ca.* 12 hr under a static blanket of nitrogen. Throughout this time, the system was protected from atmospheric moisture by an Aquasorb drying tube on the condenser. The solution was then filtered into a 500-ml erlenmeyer flask equipped with a side-arm nitrogen inlet, and the filtrate was heated to reflux. To the filtrate, which contained 1.9 g (3.4 mmol) of dissolved titanium(IV) iodide, acetylacetone (0.85 ml, 8.3 mmol) was added with a syringe through the reflux condenser while a stream of dry nitrogen was passed over the surface of the solution. Within less than 1 min, shiny, black crystals of $Ti(acac)_2I_2$ appeared. The mixture was allowed to reflux for 10 min under a static blanket of nitrogen after which time the crystals (1.3 g, 76% theoretical) were filtered, washed with three 20-ml portions of ether, and dried *in vacuo.* The crystals are small, pseudohexagonal plates which exhibit parallel extinction and strong pleochroism, being light brown when the plane of polarization is parallel to the longest axis of the plate and dark brown when the plane of polarization is perpendicular to this axis; mp 195–200° dec.

Anal. Calcd for $Ti(C_5H_7O_2)_2I_2$: C, 24.02; H, 2.82; I, 50.77; Ti, 9.58. Found: C, 24.21; H, 3.01; I, 50.63; Ti, 9.39.

An emission spectrum of $Ti(acac)_2I_2$ was run on an Ebert 3.4-m optical spectrograph. No transition elements were detected except for copper which was found at a level of 10 ppm. For this analysis the detection limits are surely <5 ppm.

Tris(2,4-pentanedionato)titanium(IV) Triiodide.—Acetylacetone (1.5 ml, 15 mmol) was added to a refluxing solution of 1.8 g of titanium(IV) iodide (3.2 mmol) in 300 ml of ether. After 5 min, dry oxygen was bubbled into the reaction mixture, which by this time contained black crystals of $Ti(acac)_2I_2$. In about 5 min, the reaction mixture began to turn red and became turbid. After 20 min, the oxygen flow was discontinued, and the resulting fine, bright red crystals (2.3 g, 97% theoretical) were filtered, washed with three 30-ml portions of ether, and dried *in vacuo;* mp 129–131° dec.

Anal. Calcd for $Ti(C_5H_7O_2)_3I_3$: C, 24.82; H, 2.92; I, 52.44; Ti, 6.60. Found: C, 24.90; H, 2.93; I, 52.68; Ti, 6.48.

$[Ti(acac)_3]I_3$ is soluble in dichloromethane and tetrahydrofuran but is insoluble in ether, benzene, and hexane. The molar conductance of a 1.00×10^{-3} *M* dichloromethane solution at 25.0° is 55 ohm^{-1} cm^2 mol^{-1}. The nmr spectrum (CH_2Cl_2, 10 g/100 ml, 37°) shows methyl and ring proton resonances at −2.27 and −6.24 ppm, respectively. The uv spectrum (CH_2Cl_2) exhibits bands at 256, 295, and 365 mμ.

Hydrolysis–Oxidation Product of Diiodobis(2,4-pentanedionato)titanium(IV).—It is important to keep the reflux time in the synthesis of $Ti(acac)_2I_2$ to a minimum. If the reflux time is in-

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[1] R. C. Fay and R. N. Lowry, *Inorg. Nucl. Chem. Lett.*, **3**, 117 (1967).
[2] R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **6**, 1512 (1967).
[3] N. Serpone and R. C. Fay, *ibid.*, **8**, 2379 (1969).
[4] D. C. Bradley and C. E. Holloway, *Chem. Commun.*, 284 (1965).
[5] D. C. Bradley and C. E. Holloway, *J. Chem. Soc. A*, 282 (1969).
[6] T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, **7**, 502 (1968).
[7] R. C. Fay and T. J. Pinnavaia, *ibid.*, **7**, 508 (1968).
[8] N. Serpone and R. C. Fay, *ibid.*, **6**, 1835 (1967).
[9] H. Weingarten, M. G. Miles, and N. K. Edelmann, *ibid.*, **7**, 879 (1968).
[10] R. N. Lowry and R. C. Fay, *Inorg. Syn.*, **10**, 1 (1967).
[11] R. C. Fay and N. Serpone, *J. Amer. Chem. Soc.*, **90**, 5701 (1968).

creased from 10 min to 12 hr, brown powders of somewhat variable composition are obtained. The brown products from several independent preparations melted with decomposition at temperatures which varied between 194 and 223°. Analytical data point to a stoichiometry close to $\mathrm{Ti(C_5H_7O_2)_2O_{0.7}I_{1.3}}$.

Anal. Calcd for $\mathrm{Ti(C_5H_7O_2)_2O_{0.7}I_{1.3}}$: C, 28.44; H, 3.34; I, 39.07; Ti, 11.34. Found (independent preparations): C, 28.78, 28.84, 26.68; H, 3.70, 3.42; 3.70; I, 38.92, 37.78; Ti, 11.28, 11.53.

The brown powders give conducting, red solutions in dichloromethane which exhibit uv maxima at 252, 292, and 360 mμ and sharp nmr resonances at −2.27 and −6.24 ppm. An additional, broad methyl resonance of variable intensity was observed in the region −2.07 to −2.17 ppm. Infrared spectra of the brown powders contain no O–H stretching bands but show a strong, broad band at 750 $\mathrm{cm^{-1}}$ which is absent in spectra of $\mathrm{Ti(acac)_2I_2}$ and $\mathrm{[Ti(acac)_3]I_3}$.

Physical Measurements. X-Ray Powder Patterns.—X-Ray powder patterns of $\mathrm{Ti(acac)_2I_2}$ were obtained with nickel-filtered Cu Kα radiation using 0.5- and 0.2-mm glass capillaries and a Debye–Scherrer camera of 360.0-mm circumference. The patterns were of rather poor quality, the diffraction arcs being weak and diffuse. The *d* spacings and visually estimated relative intensities of the distinguishable lines are listed: 7.31 (2), 6.67 (10), 6.05 (9), 3.83 (3), 3.71 (5), 3.60 (3), 3.52 (6), 3.37 (2), 3.25 (1), 3.20 (1), 2.98 (3), 2.78 (4), 2.55 (2), 2.48 (3).

Conductance Measurements.—These were made in dichloromethane solution at 25.00 ± 0.05° using previously described techniques.[2] The same solvent was employed for measurements at Dry Ice–acetone temperature (−78.5°). For the more highly conducting solutions ($\mathrm{Ti(acac)_2I_2}$ and $\mathrm{[Si(acac)_3]Br}$), the bridge frequency was 1000 cps. The molar conductances, in $\mathrm{ohm^{-1}\ cm^2\ mol^{-1}}$, are given below, followed, in parentheses, by molar concentration ($\times 10^3$). $\mathrm{Ti(acac)_2I_2}$ at 25°: 5.9 (10), 7.2 (5.0), 10.7 (2.0), 16.9 (1.0). $\mathrm{Ti(acac)_2Cl_2}$ at 25°: 0.029 (10), 0.092 (5.0), 0.034 (2.0), 0.047 (1.0). $\mathrm{[Si(acac)_3]Br}$ at 25°: 36 (10), 40 (5.0), 46 (2.5), 54 (1.3), 57 (1.0), 68 (0.50), 95 (0.10), 102 (0.050), 125 (0.010), 136 (0.0050), 176 (0.0010). $\mathrm{[Si(acac)_3]Br}$ at −78.5°: 11.9 (10), 12.1 (5.0), 13.7 (2.5), 15.0 (2.0), 21.4 (0.50), 29 (0.10), 36 (0.010), 40 (0.0050), 52 (0.0010).

Mass Spectrum.—The mass spectrum of $\mathrm{Ti(acac)_2I_2}$ was recorded with an Associated Electrical Industries MS 902 high-resolution mass spectrometer at an ionizing voltage of 70 V and an ionization chamber temperature of about 200°. The sample was introduced into the ionization chamber *via* the direct insertion lock. Perfluorokerosene was used as a mass reference.

Magnetic Resonance Spectra.—Proton nmr spectra were recorded with a Varian A-60A spectrometer using techniques described previously.[2] Chemical shifts were measured relative to an internal reference of tetramethylsilane (1% by volume).

Esr spectra were recorded with a Varian V-4502 spectrometer system having 100-kc/sec field modulation. The *g* value of $\mathrm{Ti(acac)_2I_2}$ was determined using a Harvey-Wells nmr precision gaussmeter, Model G-502, and a Hewlett-Packard frequency counter, Model 524D. The absolute number of unpaired spins was measured by the method of Hyde and Brown[12] using a Varian V-4532 dual-sample cavity and a Varian standard calibrating sample consisting of 0.1% pitch in KCl. All nmr and esr samples were contained in vacuum-sealed tubes. A 4-mm o.d. thin-walled quartz tube was used for determination of the number of unpaired spins.

Results and Discussion

Diiodobis(2,4-pentanedionato)titanium(IV) has been prepared in good yield by reaction of acetylacetone with titanium(IV) iodide in diethyl ether solution: $\mathrm{TiI_4 + 2H(acac) \rightarrow Ti(acac)_2I_2 + 2HI}$. Attempted syntheses in dichloromethane, benzene, and tetrahydrofuran resulted in the formation of oils, and use of carbon tetrachloride yielded a brown hydrolysis–oxidation product. Metathesis reactions between $\mathrm{TiI_4}$ and Na(acac) or Tl(acac) were similarly unsuccessful.

$\mathrm{Ti(acac)_2I_2}$ is obtained from ether as small, black, pseudohexagonal plates. Although the crystal form is similar to that of $\mathrm{Ti(acac)_2F_2}$ and $\mathrm{Ti(acac)_2Br_2}$,[2] the X-ray powder pattern does not provide convincing evidence for isomorphism. Like the other dihalides, solid $\mathrm{Ti(acac)_2I_2}$ must be stored under anhydrous conditions. When exposed to the atmosphere, it is converted to a white powder, presumably titanium(IV) oxide; serious hydrolysis was noted after an exposure time of 30 min.

$\mathrm{Ti(acac)_2I_2}$ is soluble in dichloromethane, benzene, and nitrobenzene but is nearly insoluble in diethyl ether, carbon tetrachloride, and saturated hydrocarbons. For the series of $\mathrm{Ti(acac)_2X_2}$ complexes, solubility decreases as X varies in the order F > Cl > Br > I. Solutions of $\mathrm{Ti(acac)_2I_2}$ are stable for only short periods of time, being very susceptible to atmospheric oxygen and water vapor with the solution turning from its initial black color to the red color of $\mathrm{I_3^-}$. In stoppered flasks, this color change was observed within times ranging from less than 5 min to 12 hr, depending on the solvent and solute concentration. Dichloromethane solutions appeared to be the most stable; consequently, this solvent was employed for most of the physical measurements. When carefully sealed under vacuum, dichloromethane solutions could be kept for several months before beginning to turn red.

The oxidation product of $\mathrm{Ti(acac)_2I_2}$ depends on the experimental conditions. If dry oxygen is passed into the $\mathrm{Ti(acac)_2I_2}$-containing reaction mixture after reaction of H(acac) with $\mathrm{TiI_4}$ in ether solution, $\mathrm{Ti(acac)_2I_2}$ is quantitatively converted to a red, crystalline material which has been shown by analysis, conductance measurements, and ir, uv, and nmr spectroscopy to be $\mathrm{[Ti(acac)_3]I_3}$. This compound behaves as a 1:1 electrolyte in dichloromethane. Its infrared and ultraviolet spectra are characteristic of the $\mathrm{Ti(acac)_3^+}$ cation with the exception of additional bands at 295 and 365 mμ in the ultraviolet and 138 $\mathrm{cm^{-1}}$ in the far-infrared owing to the $\mathrm{I_3^-}$ ion.[13] The nmr resonances of the compound are shifted to low field as expected for a positively charged species.[11] Since HI and excess H(acac) are present under the reaction conditions, the oxidation probably proceeds according to

$$\mathrm{Ti(acac)_2I_2 + HI + H(acac) + 0.5O_2 \longrightarrow [Ti(acac)_3]I_3 + H_2O}$$

If the reaction time in the synthesis of $\mathrm{Ti(acac)_2I_2}$ is increased from the usual 10 min to 12 hr, oxidation and hydrolysis take place. Under these conditions, brown powders are obtained, the compositions of which approximate $\mathrm{Ti(acac)_2O_{0.7}I_{1.3}}$. Ultraviolet spectra of these materials are qualitatively similar to the spectrum of $\mathrm{[Ti(acac)_3]I_3}$ and clearly indicate the presence of $\mathrm{I_3^-}$. Nmr spectra of the brown powders are more complex than the spectrum of $\mathrm{Ti(acac)_3^+}$, and a strong, broad band at *ca.* 750 $\mathrm{cm^{-1}}$ in the infrared spectra suggests

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[12] J. S. Hyde and H. W. Brown, *J. Chem. Phys.*, **37**, 368 (1962).

[13] A full report on the infrared and electronic spectra of $\mathrm{Ti(acac)_3^+}$, $\mathrm{Ti(acac)_2I_2}$, and related diketonate complexes of the type $\mathrm{Ti(dik)_3^+}$ and $\mathrm{Ti(dik)_2X_2}$ is in preparation.

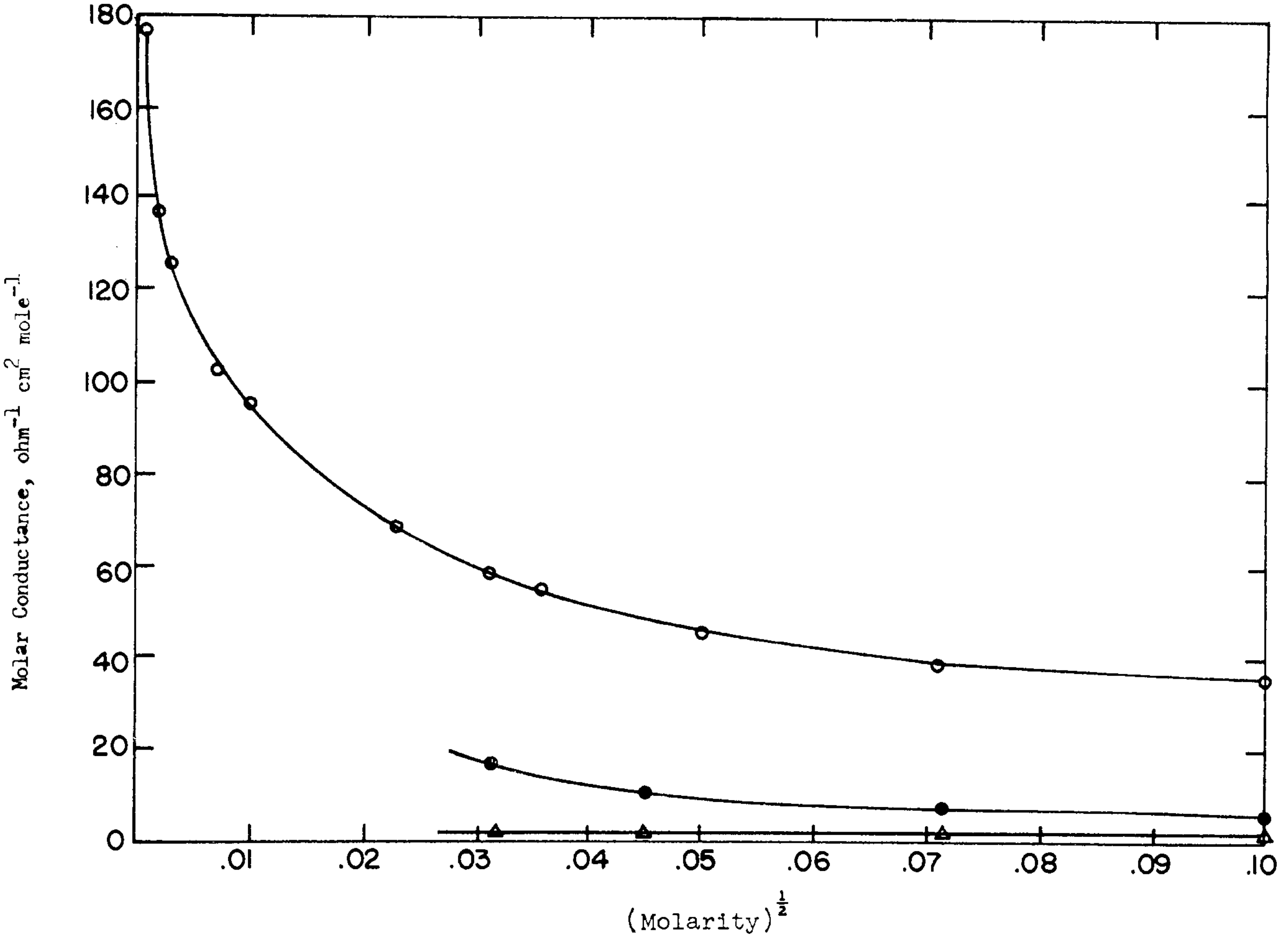

Figure 1.—Molar conductance of $[Si(acac)_3]Br$ (O—O), $Ti(acac)_2I_2$ (●—●), and $Ti(acac)_2Cl_2$ (△—△) in dichloromethane solution at 25°

that these materials contain a polymeric cation having Ti–O–Ti bridges. A similar band has been reported at *ca.* 765 cm^{-1} for $[TiO(acac)_2]_2$, the hydrolysis product of $Ti(acac)_2(OC_4H_9)_2$, which was formulated on the basis of molecular weight evidence as a dimeric species containing Ti–O–Ti bridge bonds.[14] Brown powders were also obtained in attempts to recrystallize $[Ti(acac)_3]I_3$ and when oxygen was bubbled into a suspension of $Ti(acac)_2I_2$ in wet diethyl ether.

A cryoscopic molecular weight determination on $Ti(acac)_2I_2$ in benzene solution was only partially successful because of solution instability, the measured molecular weight increasing as a function of time. The first measured value (20 min after dissolution of the complex) was 634, in fair agreement with the value of 500 calculated for $Ti(acac)_2I_2$. The mass spectrum (Table I) is entirely consistent with a monomeric $Ti(acac)_2I_2$ species in the gas phase although the molecular ion is not observed because of easy cleavage of the Ti–I bond. It is noteworthy that $Ti(acac)_3^+$ (m/e 345) is found among the more abundant ions. Apparently, ligand exchange occurs quite readily in the ion source of the mass spectrometer.

The conductance behavior of $Ti(acac)_2I_2$ in dichloromethane solution is intermediate between that of the nonelectrolyte, $Ti(acac)_2Cl_2$, and the 1:1 electrolyte, $[Si(acac)_3]Br$. Plots of the molar conductance Λ *vs.* (molarity)$^{1/2}$ are presented in Figure 1. The conductance of $Ti(acac)_2I_2$ is attributed primarily to dissociation of iodide ions

$$Ti(acac)_2I_2 \rightleftharpoons Ti(acac)_2I^+ + I^-$$

although oxidation to I_3^- may also contribute to the observed conductance.[15] For a 3 wt/vol % solution, the concentration used in the nmr experiments, Λ is 3.1

TABLE I

MASS SPECTRUM[a] OF $Ti(acac)_2I_2$

Ion	m/e[b]		Rel intens[c]
	Obsd	Calcd	
$Ti(acac)_2I^+$	372.9428	372.9414	s
$Ti(acac)_3^+$	345.0819	345.0817	s
$Ti(acac)I^+$	273.8957	273.8968	vw
$Ti(acac)_2^+$	246.0379	246.0370	vs
$TiIOH^+$	191.8541	191.8551	vw
$TiOI^+$	190.8459	190.8472	vw
$TiO(acac)^+$	162.9880	162.9874	s
$Ti(acac)^+$	146.9937	146.9925	vw
$TiO(OH)^+$	80.9449	80.9455	w
$TiOCH_3^+$	78.9656	78.9663	vw
TiO^+	63.9439	63.9428	m

[a] Only the more abundant metal-containing ions are listed. [b] Based on ^{48}Ti. [c] Abbreviations: s, strong; v, very; m, medium; w, weak.

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[14] A. Yamamoto and S. Kambara, *J. Amer. Chem. Soc.*, **79**, 4344 (1957).

[15] Ultraviolet spectra of the conductance solutions indicate that the conductance cannot be wholly accounted for by oxidation, and nmr spectra (*vide infra*) show the presence of a cationic species under conditions where no oxidation occurs.

$\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ at 25° and 1.12 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ at −78.5°. Comparison of these values with Λ *vs* (molarity)$^{1/2}$ plots for [Si(acac)$_3$]Br allows the per cent dissociation at this concentration to be estimated at 7.9 and 9.3% at 25 and −78.5°, respectively.

Perhaps the most surprising property of Ti(acac)$_2$I$_2$ is the fact that it gives no nmr spectrum at room temperature but does give an esr spectrum; nmr spectra are only observed below about 0°. The esr spectra of dichloromethane solutions (Figure 2) show a broad signal which has a g value of 1.97 ± 0.01 at 20°. A similar, but even broader signal was observed for the solid. Because the g value is in the range characteristic of titanium(III) complexes[16] and because the emission spectrum of Ti(acac)$_2$I$_2$ precludes the presence of other transition metals at concentrations >10 ppm, the esr signal is assigned to a Ti(III) species. A likely possibility, accessible by homolytic cleavage of a Ti–I bond, is Ti(acac)$_2$I. The concentration of unpaired spins in a 4.0 wt/vol % dichloromethane solution at room temperature was found to be 6.1 × 10^{19} spins/l., which means that 0.13% of the titanium is present as Ti(III).

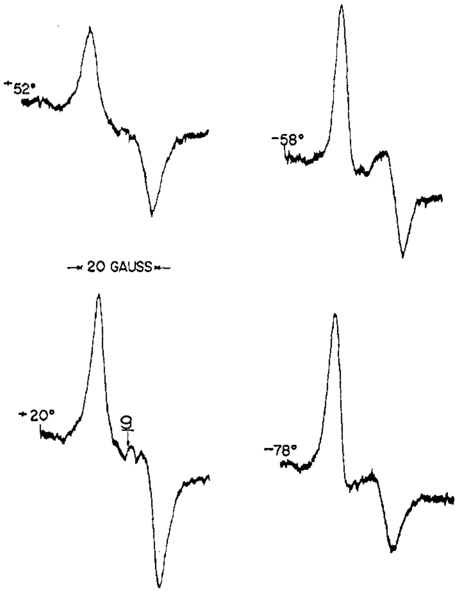

Figure 2.—Esr spectra of Ti(acac)$_2$I$_2$ in dichloromethane solution (3 g/100 ml).

The absence of an nmr spectrum at room temperature cannot be attributed to an intermolecular relaxation mechanism owing simply to the presence of a paramagnetic species in the solution because Ti(acac)$_2$I$_2$-containing solutions give normal (*i.e.*, neither broadened nor shifted) resonances at room temperature for tetramethylsilane, for the dichloromethane solvent, and even for added solutes such as [Ti(acac)$_3$]I$_3$. The disappearance of the spectrum is ascribed to a rapid rate process which exchanges acetylacetonate ligands between the diamagnetic Ti(acac)$_2$I$_2$ and paramagnetic Ti(III) environments. This process need not involve rupture of Ti–acac bonds; for example, if the Ti(III) species is Ti(acac)$_2$I, averaging of the acac environments might be accomplished by iodine atom transfer between Ti(acac)$_2$I$_2$ and Ti(acac)$_2$I. In any case, the rate of environmental averaging must be fast; the lifetime of an acac ligand in a Ti(III) environment is estimated to be $\lesssim 10^{-6}$ sec at room temperature.[17,18]

Below about 0° the nmr spectrum of Ti(acac)$_2$I$_2$ can be observed owing to a decrease in the above rate process. The methyl region of low-temperature spectra is presented in Figure 3; chemical shifts and relative intensities are given in Table II. Between −32 and −59° one observes two methyl resonances having relative intensities 10:90. The more intense, high-field line is assigned to Ti(acac)$_2$I$_2$. The low-field line has the same chemical shift as Ti(acac)$_3$$^+$, and therefore it is assigned to the cationic species resulting from electrolytic dissociation of Ti(acac)$_2$I$_2$, presumably Ti(acac)$_2$I$^+$.[19] The relative concentrations of Ti-

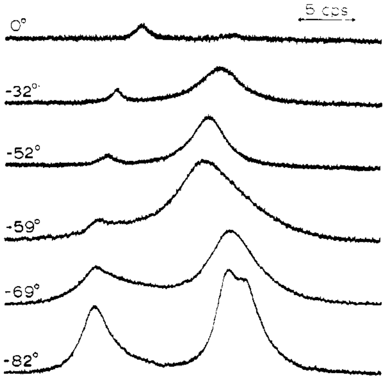

Figure 3.—Methyl regions of 60-MHz proton nmr spectra of Ti(acac)$_2$I$_2$ in dichloromethane solution (3 g/100 ml). The spectra were not all recorded at the same spectrum amplitude.

TABLE II

NMR DATA FOR Ti(acac)$_2$I$_2$ IN DICHLOROMETHANE SOLUTION[a]

Temp, °C	-CH$_3$		-CH=	
37	*b*	*b*	*b*	
0	−2.28^c	*Ca.* −2.13^c	*b*	
−32	−2.32 (10)^d	−2.15 (90)^d	−6.26^c	
−52	−2.33 (9)	−2.17 (91)	−6.32	
−59	−2.34 (10)	−2.17 (90)	−6.36	
−69	−2.35 (30)	−2.14 (70)	−6.44	−6.34
−79	−2.36 (35)	−2.15 −2.13 (65)	−6.46 (41)^d	−6.33 (59)^d
−82	−2.35 (33)	−2.15 −2.13 (67)	−5.47 (37)	−6.34 (63)
−90	−2.39 (35)	−2.18^e (65)	−6.53 (40)	−6.41 (60)

[a] Concentration 3 g/100 ml. [b] Resonance is not observed at this temperature. [c] Chemical shifts in ppm relative to tetramethylsilane. [d] Relative intensities based on total = 100. [e] Resolution of the high-field methyl doublet is lost because of viscosity broadening.

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[16] (a) H. S. Jarrett, *J. Chem. Phys.*, **27**, 1298 (1957); (b) B. R. McGarvey, *ibid.*, **38**, 388 (1963); (c) E. L. Waters and A. H. Maki, *Phys. Rev.*, **125**, 233 (1962); (d) J. C. W. Chien and C. R. Boss, *J. Amer. Chem. Soc.*, **83**, 3767 (1961); (e) S. Fujiwara and M. Codell, *Bull. Chem. Soc. Jap.*, **37**, 49 (1964).

[17] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 221. Our estimate assumes a large chemical shift between Ti(acac)$_2$I$_2$ and the paramagnetic Ti(III) species[18] and assumes that the Ti(acac)$_2$I$_2$ resonances would be too broad to observe when the line width parameter $T_2 \gtrsim 10^3$ radians/sec.

[18] D. R. Eaton, *J. Amer. Chem. Soc.*, **87**, 3097 (1965).

[19] Assignment of the low-field line to Ti(acac)$_3$$^+$ or to the cation of the hydrolysis–oxidation product can be ruled out. Even at a relative concentration of 10%, these ions would give an observable methyl resonance at −2.27 ppm in the room-temperature spectrum. Furthermore, spectra of Ti(acac)$_2$I$_2$–[Ti(acac)$_3$]I$_3$ mixtures give three ring proton signals at −82° (−6.47, −6.38, and −6.35 ppm) while in the −82° spectrum of Ti(acac)$_2$I$_2$ (Table II) the Ti(acac)$_3$$^+$ line at −6.38 ppm is completely absent. We believe that oxidation has been avoided in preparation of the nmr solutions.

(acac)$_2$I$^+$ and Ti(acac)$_2$I$_2$ obtained from the nmr spectra are in excellent agreement with the figure of 8–9% dissociation derived from the conductance measurements, thus confirming the assignment of the methyl resonances. It is interesting to note that the Ti(acac)$_2$I$_2$ methyl resonance broadens with increasing temperature at lower temperatures than the Ti(acac)$_2$I$^+$ resonance (*cf.* the 0° spectrum in Figure 3). Apparently the rate of acac exchange between the Ti(III) and Ti(IV) environments is somewhat slower for the positively charged Ti(IV) complex. The ring proton region shows only one resonance line at temperatures above *ca.* $-67°$; the Ti(acac)$_2$I$_2$ and Ti(acac)$_2$I$^+$ signals either coincide, or the latter is too weak to be observed.

Below $-52°$ the Ti(acac)$_2$I$_2$ methyl resonance broadens and then splits at *ca.* $-64°$ into two lines having relative intensities 35:65. The less intense, low-field line coincides with the Ti(acac)$_2$I$^+$ resonance. At still lower temperatures, the more intense, high-field line is partially resolved into two lines, which are separated by 0.023 ppm. This resolution is reproducible and was observed at -79, -82, and $-85°$. The ring proton resonance also broadens below $-52°$ and splits into two lines at *ca.* $-67°$. The three methyl and two ring proton resonances at the lower temperatures indicate that Ti(acac)$_2$I$_2$ exists in solution as a mixture of *cis* and *trans* isomers. The methyl resonances can be assigned by reference to the low-temperature spectra of the analogous Ti(acac)$_2$X$_2$ complexes, X = F, Cl, or Br, for which the chemical shifts between the two methyl resonances of the *cis* isomer are 0.04, 0.11, and 0.15 ppm, respectively.[2] One therefore expects a chemical shift >0.15 ppm for *cis*-Ti(acac)$_2$I$_2$, from which it follows that the lowest field methyl resonance must be assigned to the *cis* isomer. One component of the high-field doublet must be the other resonance of the *cis* isomer; the other component is assigned to the *trans* isomer. From the relative intensities of the methyl resonances, the relative concentrations can be estimated to be ~10% Ti(acac)$_2$I$^+$, ~50% *cis*-Ti(acac)$_2$I$_2$, and ~40% *trans*-Ti(acac)$_2$I$_2$. Assignment of the ring proton resonances is less certain because the *cis* and *trans* isomers have comparable concentrations; however, the assignment most consistent with the relative intensities identifies the low-field –CH= line with the *trans* isomer and the high-field line with the *cis* isomer, perhaps superposed on the signal due to Ti(acac)$_2$I$^+$.

Coalescence of the Ti(acac)$_2$I$_2$ methyl and ring proton signals at *ca.* -64 and $-67°$, respectively, indicates rapid *cis–trans* isomerization as well as rapid exchange of methyl groups between the two nonequivalent sites of the *cis* isomer. Rough estimates of the mean residence time τ, based on the two-site exchange case,[20] are 0.03 sec at $-67°$ for *cis–trans* isomerization (estimated from the ring proton region) and 0.02 sec at $-64°$ for exchange of methyl groups. Thus, Ti(acac)$_2$I$_2$ is somewhat less rigid than the corresponding difluoro, dichloro, and dibromo complexes.[2]

It is noted in passing (*cf.* Figure 3 and Table II) that the centers of gravity of the methyl and –CH= resonances shift to lower field with decreasing temperature. These shifts, which are superimposed upon the line-broadening effects already discussed, are probably due to increasing solvation at the lower temperatures. Similar shifts have been observed for Ti(acac)$_2$Br$_2$ and Co(acac)$_3$ (*cf.* Table III), suggesting that temperature-dependent, low-field shifts may be quite general for metal acetylacetonates.

TABLE III

CHEMICAL SHIFT DATA FOR Ti(acac)$_2$Br$_2$ AND Co(acac)$_3$ IN DICHLOROMETHANE SOLUTION[a]

Temp, °C	Ti(acac)$_2$Br$_2$[b]			Co(acac)$_3$[c]	
	–CH$_3$		–CH=	–CH$_3$	–CH=
37	−2.14		−6.04	−2.14	−5.54
0	−2.17		−6.11	−2.16	−5.61
−30	−2.19		−6.16	−2.19	−5.65
−63	−2.31	−2.15	−6.24	−2.22	−5.71
−82	−2.33	−2.18	−6.29	−2.25	−5.77

[a] Chemical shifts are in ppm relative to tetramethylsilane. [b] Concentration 2.43 g/100 ml. [c] Concentration 2.14 g/100 ml.

Further evidence for the existence of a mixture of *cis*- and *trans*-Ti(acac)$_2$I$_2$ in dichloromethane solution comes from the infrared spectra,[13] which show a single metal–oxygen stretching band in the 450–510-cm^{-1} region for *cis*-Ti(acac)$_2$X$_2$ (X = F, Cl, Br), but three overlapping bands for Ti(acac)$_2$I$_2$. Although *trans*-M(acac)$_2$X$_2$ complexes are uncommon, a few other examples are known. The *trans* configuration has been found for Re(acac)$_2$Cl$_2$ in the solid state,[21] and it has been suggested that Si(acac)$_2$Cl$_2$ is *trans* in solution.[22] There is also evidence that some of the dihalobis(β-diketonato)germanium(IV) complexes have a *trans* structure.[23]

It is significant that the –CH= proton resonance of *trans*-Ti(acac)$_2$I$_2$, as well as that of the *cis* isomer, is shifted to low field relative to the –CH= resonances of neutral, nonpolar M(acac)$_n$ complexes. The same result has been found for recently studied *cis*- and *trans*-Ge(β-dik)$_2$Cl$_2$ complexes.[23] Since low-field shifts for the *trans* isomer are not expected on the basis of an electric field model,[3,24] these shifts support the view[25] that factors other than electric field effects are important in determining the chemical shifts of M(acac)$_2$X$_2$ complexes. It is apparent that inductive effects[23a,26] are of principal importance.

Conclusion

It has been shown that dichloromethane solutions of Ti(acac)$_2$I$_2$ contain ~50% *cis*-Ti(acac)$_2$I$_2$, ~40% *trans*-Ti(acac)$_2$I$_2$, ~10% of an electrolytic dissociation product, presumably [Ti(acac)$_2$I]$^+$I$^-$, and 0.13% of a paramagnetic Ti(III) species. The behavior of Ti(acac)$_2$I$_2$ is therefore strikingly different from that of

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