

wise destabilize the *cis* structures. π bonding also would decrease the positive charge on the central tin atom and make it less susceptible to nucleophilic attack. Such a suggestion explains the compounds' unusual reluctance to hydrolyze. Quite evidently, the suggestion that ($p \rightarrow d$) π overlap is important between

tin and halogen atoms is consistent with the observed stability of the *cis* isomers of type X_2SnI_2 .

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Stereochemistry and Lability of Dihalobis(β -diketonato)titanium(IV) Complexes. I. Acetylacetonates¹

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The preparation and characterization of dihalobis(acetylacetonato)titanium(IV) complexes, $Ti(acac)_2X_2$ ($X = F, Cl, Br$), is reported. X-Ray powder patterns suggest that the crystalline solids may be isomorphous. Molecular weight, conductivity, and proton nmr data demonstrate that the complexes are monomeric nonelectrolytes which exist in solution as *cis* geometrical isomers. Variable temperature nmr spectra show that the acetylacetonate rings undergo rapid configurational changes which exchange acetylacetonate methyl groups between the two nonequivalent sites of the *cis* isomer. First-order rate constants, extrapolated to 25°, for exchange of methyl groups, activation energies, and entropies of activation have been determined to be, respectively, $1.6 \times 10^4 \text{ sec}^{-1}$, $11.6 \pm 0.5 \text{ kcal/mole}$, and $-2.4 \pm 2.3 \text{ eu}$ ($X = F$); $6.7 \times 10^2 \text{ sec}^{-1}$, $11.2 \pm 0.6 \text{ kcal/mole}$, and $-10.0 \pm 2.3 \text{ eu}$ ($X = Cl$); $2.3 \times 10^3 \text{ sec}^{-1}$, $11.6 \pm 0.4 \text{ kcal/mole}$, and $-6.3 \pm 1.6 \text{ eu}$ ($X = Br$). Possible mechanisms for the configurational changes are discussed briefly.

Introduction

The structure of the product obtained from the reaction of acetylacetone (Hacac) with titanium(IV) chloride has been of considerable interest. This reaction was first studied in ether solution by Rosenheim,² who formulated the product as the ether addition compound, $Ti(acac)Cl_3 \cdot (C_2H_5)_2O$. Dilthey³ repeated Rosenheim's preparation, but Dilthey's analytical data indicated that the composition of the product was $Ti(acac)_2Cl_2$. The absence of ether was confirmed by the fact that the same product was obtained when the reaction was carried out in glacial acetic acid or in chloroform. Dilthey suggested the ionic structure, $[Ti(acac)_3]_2[TiCl_6]$, on the basis of similarities in the chemical behavior of the titanium compound and the analogous silicon compound, $[Si(acac)_3]Cl \cdot HCl$.⁴ In particular, both compounds react with certain anhydrous metal chlorides, for example, iron(III) chloride and platinum(IV) chloride, yielding "double salts" of the type $[M(acac)_3][FeCl_4]$ and $[M(acac)_3]_2[PtCl_6]$.

Although the existence of the $[Ti(acac)_3]^+$ cation in double salts such as $[Ti(acac)_3][FeCl_4]$ is now well established,⁵⁻⁸ the ionic formulation, $[Ti(acac)_3]_2[TiCl_6]$, for the original reaction product appears to be incor-

rect. Mehrotra and coworkers⁹⁻¹¹ have contended, on the basis of chemical, molecular weight, and conductivity evidence, that the product should be formulated as the monomeric nonelectrolyte, $[Ti(acac)_2Cl_2]$. Mehrotra's conclusion has been confirmed by Cox, Lewis, and Nyholm,⁶ who have studied an entire series of dichlorobis(β -diketonato)metal complexes.¹² In view of the considerable evidence for the nonelectrolyte structure, it is unfortunate that the ionic formulation appears in the recent literature.¹³

We, also, have been investigating the constitution of $Ti(acac)_2Cl_2$. In this connection, we have prepared and characterized the difluoro and dibromo analogs. The present paper reports the results of molecular weight, conductance, X-ray powder diffraction, and nmr studies of the $Ti(acac)_2X_2$ complexes ($X = F, Cl, Br$). The nmr results are especially significant because they reveal the molecular stereochemistry and kinetic lability of the complexes.

(5) R. J. Woodruff, J. L. Marini, and J. P. Fackler, Jr., *Inorg. Chem.*, **3**, 687 (1964).

(6) M. Cox, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 6113 (1964).

(7) W. K. Ong and R. H. Prince, *J. Inorg. Nucl. Chem.*, **27**, 1037 (1965).

(8) G. M. Bancroft, A. G. Maddock, W. K. Ong, and R. H. Prince, *J. Chem. Soc., Sect. A*, 723 (1966).

(9) K. C. Pande and R. C. Mehrotra, *Chem. Ind. (London)*, 1198 (1958).

(10) D. M. Puri and R. C. Mehrotra, *J. Less-Common Metals*, **3**, 247 (1961).

(11) D. M. Puri, K. C. Pande, and R. C. Mehrotra, *ibid.*, **4**, 481 (1962).

(12) It should be noted, however, that there is a large quantitative discrepancy between the conductivity results of Mehrotra¹¹ and Cox.⁶ This discrepancy will be discussed in more detail in the Results and Discussion section.

(13) V. Doron, *Inorg. Syn.*, **7**, 50 (1963). See also, however, the correction, *ibid.*, **8**, 37 (1966).

(1) For preliminary reports of some of these results see (a) R. C. Fay, T. J. Pinnavaia, N. Serpone, and R. N. Lowry, Proceedings of the 9th International Conference on Coordination Chemistry, St. Moritz-Bad, Switzerland, 1966, p 486; (b) R. C. Fay and R. N. Lowry, *Inorg. Nucl. Chem. Letters*, **3**, 117 (1967).

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

(3) W. Dilthey, *ibid.*, **37**, 588 (1904).

(4) W. Dilthey, *ibid.*, **36**, 923 (1903).

Experimental Section

Reagents.—Acetylacetone (Matheson Coleman and Bell, bp 136–140°), titanium tetrafluoride (K & K Laboratories), and titanium tetrachloride (Matheson Coleman and Bell) were used as purchased without further purification. Titanium(IV) bromide was prepared by the method of Young.¹⁴

Benzene, hexane, dichloromethane, and deuteriochloroform were dried by refluxing for at least 12 hr over calcium hydride. Acetonitrile was dried by refluxing over phosphorus(V) oxide. Nitrobenzene was purified for conductance measurements by an abbreviation of the procedure of Taylor and Kraus.¹⁵ This solvent was washed three times with 1:1 sulfuric acid, once with water, several times with 1 *M* sodium hydroxide until the washings were no longer colored, and then again with water. The nitrobenzene was stored overnight over Linde molecular sieves (Type 4A, 1/16-in. pellets). It was then distilled under reduced pressure (1 mm) from a fresh batch of molecular sieves. The specific conductance of the purified solvent was $<4 \times 10^{-8}$ ohm⁻¹ cm⁻¹.

General Techniques.—Since the Ti(acac)₂X₂ complexes are readily hydrolyzed, especially in solution, all syntheses and subsequent handling of the compounds were conducted under anhydrous conditions in a dry nitrogen atmosphere. Filtrations were performed using a modified, fritted glass funnel similar to that described by Holah.¹⁶ Recrystallizations were carried out under nitrogen in a glass-stoppered erlenmeyer flask equipped with a side-arm nitrogen inlet. All glassware was dried at ca. 140° and was allowed to cool in a stream of dry nitrogen. Samples and solutions for physical measurements were prepared in a nitrogen glove bag.

Difluorobis(2,4-pentanedionato)titanium(IV).—Acetylacetone (8.8 ml, 0.086 mole) was added to a suspension of titanium(IV) fluoride (4.35 g, 0.351 mole) in 150 ml of dichloromethane. The reaction mixture was allowed to reflux for 12 hr with a slow stream of dry nitrogen passing through the solution to aid in dispelling the evolved hydrogen fluoride. The resulting yellow solution was filtered to remove any undissolved residue. The solution was then boiled down to ca. 75 ml, and hexane was added with stirring until the product began to crystallize. After crystallization was complete (ca. 12 hr), the product was filtered and dried *in vacuo* at room temperature. The crude product (7.0 g, 70% theoretical) was recrystallized twice from dichloromethane–hexane. The crystals (Figure 1) are yellow plates which exhibit parallel extinction and a trace of pleochroism; mp 165–166°.

Anal. Calcd for Ti(C₅H₇O₂)₂F₂: C, 42.27; H, 4.97; F, 13.38; Ti, 16.86; mol wt, 284. Found: C, 42.22; H, 4.70; F, 13.61; Ti, 16.68; mol wt, 301; molar conductance Δ_M , <0.04 ohm⁻¹ cm² mole⁻¹.

Muetterties¹⁷ has reported a compound which has similar composition but a much lower melting point, 124° dec.

Dichlorobis(2,4-pentanedionato)titanium(IV).—Titanium(IV) chloride (5.8 ml, 0.053 mole) was added slowly to a solution of acetylacetone (13.1 ml, 0.128 mole) in 150 ml of dichloromethane. The red solution was purged for 20 min with a slow stream of dry nitrogen to remove evolved hydrogen chloride. The solution was then boiled down to ca. 75 ml, and 100 ml of hexane was added. After 4 hr the red-orange product was filtered and dried *in vacuo*. The yield of crude product was 15.1 g (90%). Recrystallization from dichloromethane–hexane gave tiny red-orange plates; mp 191–192° dec. A few of the plates exhibited parallel extinction and some of the same angles found for the other dihalides (Figure 1). However, most of the crystals were parallelogram-shaped plates. Some of these gave symmetric extinction; others gave oblique extinction. The crystals showed marked pleochroism, being red-orange when the plane of polarization was more nearly parallel to the length of the plate, and

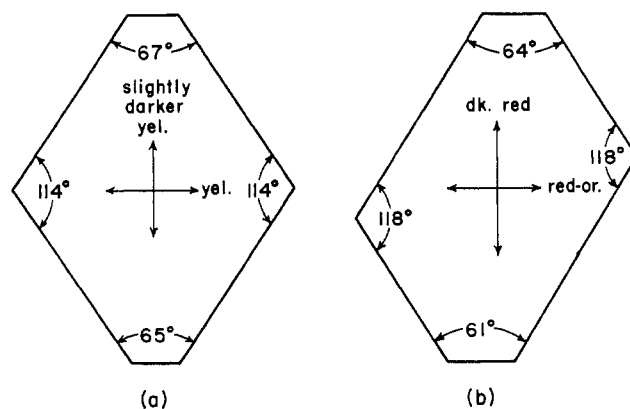


Figure 1.—Crystals of (a) Ti(acac)₂F₂ and (b) Ti(acac)₂Br₂. Angles are accurate to $\pm 2^\circ$.

yellow-orange when the plane of polarization was more nearly perpendicular to this direction.

Anal. Calcd for Ti(C₅H₇O₂)₂Cl₂: C, 37.89; H, 4.45; mol wt, 317. Found: C, 38.10; H, 4.46; mol wt, 306; Δ_M , 0.57 ohm⁻¹ cm² mole⁻¹.

The observed melting point is in agreement with that of Cox, *et al.*,⁶ (190–193°) but does not agree with the behavior reported by Doron,¹⁸ who states that, upon heating, the compound turns from red-orange to yellow and decomposes at ca. 230°.

Dibromobis(2,4-pentanedionato)titanium(IV).—Titanium(IV) bromide (9.72 g, 0.0264 mole) was added to a solution of acetylacetone (6.2 ml, 0.061 mole) in 150 ml of dichloromethane. The reaction mixture was swirled until the titanium(IV) bromide dissolved. After purging for 20 min with dry nitrogen, the dark red solution was filtered, then boiled down to ca. 75 ml, and 100 ml of hexane was added. After 4 hr the dark red product was filtered and dried at room temperature *in vacuo*; yield, 9.1 g (85%). Recrystallization from dichloromethane–hexane gave tiny, pseudo-hexagonal plates (Figure 1) which exhibit parallel extinction and very strong pleochroism; mp 243–244° dec.

Anal. Calcd for Ti(C₅H₇O₂)₂Br₂: C, 29.59; H, 3.48; Br, 39.37; Ti, 11.80; mol wt, 406. Found: C, 29.74; H, 3.49; Br, 39.27; Ti, 11.97; mol wt, 401; Δ_M , 0.66 ohm⁻¹ cm² mole⁻¹.

Hydrolysis.—When exposed to the atmosphere, the crystalline solids showed pitting of the crystal faces, loss of sharp extinction, and loss of color. The dibromo and dichloro complexes eventually were converted to an opaque white powder, presumably titanium(IV) oxide. Serious hydrolysis was noted after the following exposure times: 1–3 days (X = F), 1–2 days (Cl), 1 hr (Br). The dibromide was almost completely hydrolyzed in 2 hr; the dichloride, in ca. 5 days. The difluoride was only partially hydrolyzed even after 10 days.

Ten-milliliter samples of acetonitrile solutions of the complexes (1.0×10^{-2} *M*) were treated with 50 μ l of water. Immediate turbidity was observed in the Ti(acac)₂F₂ solution. The Ti(acac)₂Cl₂ and Ti(acac)₂Br₂ solutions immediately yielded a white precipitate, presumably titanium(IV) oxide.

Reaction with Silver Ion.—Ten-milliliter samples of dry nitrobenzene solutions of the Ti(acac)₂X₂ complexes (1.0×10^{-3} *M*) were treated with 0.20 ml of 2 *M* silver nitrate in dry acetonitrile. Complete precipitation of silver halide and decolorization of the solutions occurred immediately.

Physical Measurements. Melting Points.—Melting points were measured with a Thomas-Hoover melting point apparatus. The thermometer was calibrated, and reported melting points are corrected.

Molecular Weights.—Molecular weights were determined in benzene solution at 37° by vapor pressure osmometry using a Mechrolab Model 301A osmometer equipped with an inert gas attachment. All measurements were made in an atmosphere of dry nitrogen. Before each run the vapor wick was freed of moisture by heating overnight *in vacuo* at ca. 136°. The instrument was calibrated with benzil.

(14) R. C. Young, *Inorg. Syn.*, **2**, 114 (1946).

(15) E. G. Taylor and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 1731 (1947).

(16) D. G. Holah, *J. Chem. Educ.*, **42**, 561 (1965).

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

Conductance Measurements.—Conductance measurements were made in nitrobenzene solution ($1.0 \times 10^{-3} M$) at $25.00 \pm 0.05^\circ$ using an Industrial Instruments Model RC 16B2 conductivity bridge (accuracy $\pm 1\%$) and a Freas-type solution cell with bright platinum electrodes. The bridge frequency was 60 cps. The cell was calibrated with 0.01000 *N* potassium chloride using a Shedlovsky variable-frequency bridge operating at a frequency of 10,000 cps.¹⁸ The cell constant was 0.1090 cm^{-1} .

Nuclear Magnetic Resonance Spectra.—Proton nmr spectra were recorded with a Varian A-60 spectrometer at 60.000 Mc. Spectra were obtained in the temperature range $+60$ to -85° using Varian variable temperature accessory Model V-6057. The magnetic field sweep of the instrument was checked against the chemical shift of a 2% (by volume) solution of benzene in carbon tetrachloride¹⁹ or by the audiofrequency side-band technique. Temperatures were determined before and after running a spectrum by measuring the chemical shift between the non-equivalent protons of methanol.

X-Ray Powder Patterns.—X-Ray powder patterns were obtained with nickel-filtered Cu $K\alpha$ radiation using 0.5-mm glass capillaries and a Debye-Scherrer camera of 360.0 mm circumference. The *d* spacings and visually estimated relative intensities are listed in Table I.

TABLE I
X-RAY POWDER DIFFRACTION DATA

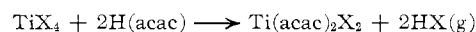
Ti(acac) ₂ F ₂	Ti(acac) ₂ Cl ₂	Ti(acac) ₂ Br ₂
7.28 ^a (0.5) ^b	...	7.10 (2)
...	6.33 (1)	...
6.54 (10)	6.37 (10)	6.29 (10)
6.14 (3)
...	5.85 (4)	5.79 (2)
5.46 (2)	...	5.45 (2)
5.16 (3)
4.20 (0.5)	4.10 (2)	4.15 (0.5)
3.99 (4)	3.97 (1)	3.97 (0.5)
3.90 (4)
3.72 (0.5)	3.83 (2)	3.76 (2)
3.61 (0.5)
3.48 (5)	3.43 (5)	3.44 (4)
...	...	3.33 (1)
3.26 (1)	3.21 (1)	3.16 (1)
3.15 (2)
3.05 (0.5)	3.06 (1)	...
2.99 (1)	...	2.89 (1)
2.81 (1)
2.71 (1)	2.72 (2)	2.76 (2)
2.60 (1)	2.63 (1)	2.65 (2)
2.49 (2)	2.50 (0.5)	2.48 (2)
...	2.40 (1)	...
...	2.36 (0.5)	2.36 (1)
...	2.30 (1)	...
2.27 (2)	2.26 (1)	2.26 (0.5)
2.19 (1)	2.18 (2)	2.22 (2)
2.00 (1)	2.03 (0.5)	2.03 (2)
...	1.986 (0.5)	...
1.920 (2)	1.901 (0.5)	1.916 (1)
1.855 (1)	1.855 (0.5)	1.867 (1)
1.808 (1)	1.815 (0.5)	...

^a *d*_{hkl}. ^b Visually estimated relative intensities.

Results and Discussion

Dihalobis(acetylacetonato)titanium(IV) complexes (halogen = fluorine, chlorine, and bromine) can be prepared in high yield by reaction of acetylacetone and

anhydrous titanium(IV) halides in dichloromethane solution.



The complexes are soluble in dichloromethane, chloroform, acetonitrile, acetone, and benzene, but are nearly insoluble in saturated hydrocarbons. The solids are attacked by water, and in solution, the complexes are hydrolyzed almost immediately. The ease of hydrolysis appears to increase in the order $\text{X} = \text{F} < \text{Cl} < \text{Br}$. It is imperative that these compounds be handled under anhydrous conditions.

X-Ray powder patterns of the crystalline solids are very similar. The *d* spacings and relative intensities (Table I) suggest that the complexes are probably isomorphous or nearly isomorphous. However, we hesitate to draw a definite conclusion since there are some differences in the diffraction patterns and since microscopic observations indicate that Ti(acac)₂Cl₂ most commonly exhibits a crystal form which is different from that of Ti(acac)₂F₂ and Ti(acac)₂Br₂. The difluoride and dibromide give the same crystal form, same type of extinction, and same pleochroism (Figure 1). It is most likely that these two complexes are isomorphous.

Molecular weight measurements in benzene solution indicate that the complexes are monomeric. Molar conductances in nitrobenzene ($< 1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$) are typical of values for nonelectrolytes in this solvent; they are much smaller than the conductances expected for 1:1 or 2:1 electrolytes (18–30 and *ca.* 60 $\text{ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$, respectively).²⁰ Infrared spectra in the 1250–1750 cm^{-1} region indicate that all acetylacetonate carbonyl groups are coordinated.²¹ Therefore, the compounds are formulated as neutral, six-coordinated complexes of the type [Ti(acac)₂X₂].

The molar conductance obtained in this work for Ti(acac)₂Cl₂ ($0.57 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$) is considerably lower than previously reported values. Mehrotra and co-workers¹¹ reported values of 6.7–8.6 (units not specified, but presumably $\text{ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$) for 1×10^{-3} to $3 \times 10^{-3} M$ nitrobenzene solutions. These values are much larger than expected for a nonelectrolyte, and they do not vary monotonically with concentration. Cox, Lewis, and Nyholm⁶ obtained a Λ_M of $1.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ for a $10^{-3} M$ nitrobenzene solution. We suggest that discrepancies among the various Λ_M values are due to partial hydrolysis. Although we have employed carefully dried nitrobenzene, our measurements exhibited significant time dependence. During a period of *ca.* 3 hr after preparation of solutions, Λ_M increased by *ca.* 25%. Use of different batches of nitrobenzene affected the Λ_M values by as much as a factor of two. Since hydrolysis appears to increase Λ_M , our conductances should be regarded as upper limits.

The small, finite conductances of the Ti(acac)₂X₂

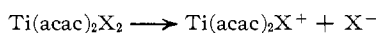
(20) E. G. Taylor and C. A. Krauss, *J. Am. Chem. Soc.*, **69**, 1731 (1947); G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 4433 (1961); D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *Inorg. Chem.*, **1**, 239 (1962).

(21) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 217.

(18) We thank Dr. J. Lind for this measurement.

(19) G. V. D. Tiers, "NMR Summary," Minnesota Mining and Manufacturing Co., St. Paul, Minn., Jan 15, 1962.

solutions may be due, at least in part, to dissociation of halide ions.



However, even for the dibromide, which appears to be most dissociated, the apparent dissociation in 10^{-3} M solutions is less than 3%. It is interesting to note that halogen is readily precipitated from these solutions as silver halide even though the complexes are only slightly ionized.²²

Stereochemistry.—The stereochemistry of the $\text{Ti}(\text{acac})_2\text{X}_2$ complexes was investigated by nmr spectroscopy. The two possible octahedral isomers are shown in Figure 2. The *cis* isomer possesses only a twofold rotation axis; this isomer has two nonequivalent sets of methyl groups (a and b in Figure 2) but only one ring proton. In the *trans* isomer (point group D_{2h}), there is a single methyl and a single ring proton environment.

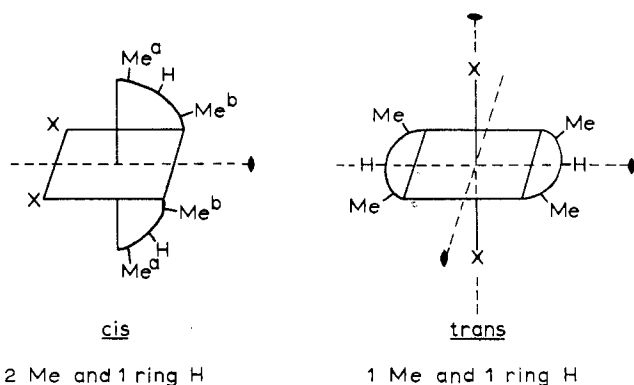


Figure 2.— $\text{M}(\text{acac})_2\text{X}_2$ *cis* and *trans* isomers.

At room temperature, proton spectra reveal one methyl and one ring proton resonance. Chemical shifts are listed in Table II. As temperature is lowered, the methyl resonance broadens and then splits into two equally intense lines. This behavior is shown for the dichloride and dibromide in Figure 3. Throughout the temperature region in which the methyl resonances coalesce, the ring proton resonance remains sharp. The low-temperature two-line methyl and one-line ring proton spectra indicate that the complexes have the *cis* configuration in solution, at least at low temperatures. Coalescence of the two methyl resonances is due to a rapid exchange process which interchanges methyl groups between the two nonequivalent sites of the *cis* isomer. The ring proton resonance remains sharp because the *cis* isomer has only one ring proton environment; methyl group exchange does not alter the environment of the ring proton.

Our results are in accord with recent studies of related bis-acetylacetonato complexes of tetravalent

(22) Ready precipitation of silver chloride has recently been interpreted as confirmatory evidence for almost complete ionization of $\text{Zr}(\text{acac})_3\text{Cl}$.²³ Such an interpretation is dubious since similar precipitation in the case of the weakly dissociated $\text{Ti}(\text{acac})_2\text{X}_2$ complexes indicates that there is no simple relationship between degree of ionization and ease of silver halide precipitation. Halide could be precipitated from weakly dissociated complexes *via* rapid halide dissociation or *via* direct attack on the complex by silver ion.

(23) V. Doron, R. K. Belitz, and S. Kirschner, *Inorg. Syn.*, **8**, 38 (1966).

TABLE II
CHEMICAL SHIFT DATA^a

Compound	Dichloromethane			Deuteriochloroform	
	—CH=	—CH ₃	—F	—CH=	—CH ₃
$\text{Ti}(\text{acac})_2\text{F}_2$	-5.89	-2.08	-232.7	-5.87	-2.10
$\text{Ti}(\text{acac})_2\text{Cl}_2$	-6.01	-2.14	...	-6.00	-2.16
$\text{Ti}(\text{acac})_2\text{Br}_2$	-6.04	-2.13	...	-6.01	-2.15

^a Proton shifts are in ppm (± 0.01) relative to an internal reference of tetramethylsilane (1% by volume). The fluorine shift is in ppm (± 0.8) relative to an internal reference of CFCl_3 (5% by volume). Concentration of compounds is 10 g/100 ml of solvent except for the less soluble $\text{Ti}(\text{acac})_2\text{Br}_2$, where concentrations are 6.0 g/100 ml of CH_2Cl_2 and 3.3 g/100 ml of CDCl_3 . Temperature is 37° (H^1) and 34° (F^{19}).

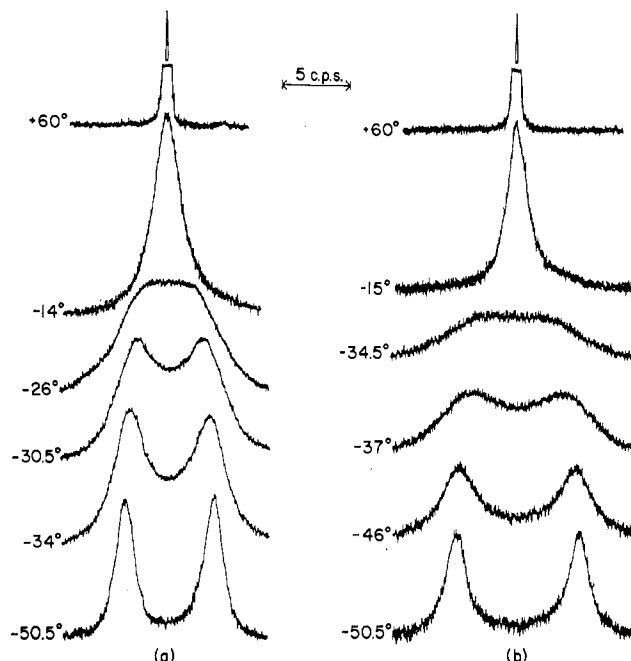


Figure 3.—Methyl region of proton nmr spectra for (a) $\text{Ti}(\text{acac})_2\text{Cl}_2$ and (b) $\text{Ti}(\text{acac})_2\text{Br}_2$ in dichloromethane solution.

metals. Although $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$ ^{24,25} and $(\text{CH}_3)_2\text{Pb}(\text{acac})_2$ ²⁴ have the *trans* configuration, all dihalo compounds of the type $\text{M}(\text{acac})_2\text{X}_2$ which have been investigated have the halogen atoms in *cis* positions. The *cis* structure has been demonstrated for $\text{Sn}(\text{acac})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$)^{26,27} and $\text{Ge}(\text{acac})_2\text{Cl}_2$.²⁷ The dialkoxide complexes, $\text{Ti}(\text{acac})_2(\text{OR})_2$, also exist in the *cis* configuration.²⁸ For *cis*- $\text{Ti}(\text{acac})_2(\text{OR})_2$ ^{28,29} and *cis*- $\text{Sn}(\text{acac})_2\text{Cl}_2$ ³⁰ exchange processes result in temperature-dependent collapse of the two methyl resonances.

The low-temperature nmr spectra of the $\text{Ti}(\text{acac})_2\text{X}_2$ complexes unequivocally exclude appreciable concentrations of the *trans* isomer. However, since observed spectra above the coalescence temperatures could be time-averaged spectra of a rapidly isomerizing *cis*-*trans* mixture and since ΔH for *cis* \rightarrow *trans* isomerization is probably positive, we must seek additional evi-

(24) Y. Kawasaki, T. Tanaka, and R. Okawara, *Bull. Chem. Soc. Japan*, **37**, 903 (1964).

(25) M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.*, **87**, 1909 (1965).

(26) J. A. S. Smith and E. J. Wilkins, *Chem. Commun.*, 381 (1965).

(27) J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc., Sect. A*, 1749 (1966).

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

(29) D. C. Bradley and C. E. Holloway, ref 1a, p 483. These workers also report kinetic data for $\text{Ti}(\text{acac})_2\text{Cl}_2$.

(30) J. W. Faller and A. Davison, *Inorg. Chem.*, **6**, 182 (1967).

dence in order to exclude *trans* isomers above the coalescence temperatures. Smith and Wilkins have pointed out that the ring proton resonances of *cis*-Sn(acac)₂X₂ and *cis*-Ge(acac)₂Cl₂ are shifted to lower field by *ca.* 0.3 ppm relative to the resonances of symmetrical, nonpolar metal acetylacetonates.²⁷ The low-field shifts were accounted for in terms of an intramolecular electric field which arises from the molecular dipole moment of the highly polar *cis* isomers. Low-field shifts are not found and are not expected for *trans* isomers since *trans* isomers have no molecular dipole moment component along the C-H bond.

In the case of the Ti(acac)₂X₂ complexes, the ring proton resonances at room temperature (Table II) exhibit very large downfield shifts (*ca.* 0.5 ppm relative to symmetrical, nonpolar metal acetylacetonates²⁷). These shifts indicate that the complexes exist largely in the *cis* configuration. If there were a labile *cis* ⇌ *trans* equilibrium which shifts significantly to the right with increasing temperature, we should see corresponding upfield shifts of the time-averaged CH proton resonances. Observed shifts (in dichloromethane solution) on going from the coalescence temperatures to +37° are less than 0.02 ppm. Therefore, we conclude that throughout the temperature range *ca.* -70 to +37°, no appreciable concentration of the *trans* isomer is present. This conclusion is supported by very broad Ti-X stretching vibrations in infrared spectra of the difluoride and dichloride in dichloromethane solution.^{1b} Infrared spectra of the crystalline solids also favor the *cis* structure.^{1b}

Kinetics of Methyl Group Exchange.—The interchange of methyl groups between the nonequivalent environments of the *cis* isomer is an example of a two-site exchange process. The populations of the two sites A and B are equal, and therefore methyl groups have the same mean residence time in each site, *i.e.*, $\tau_A = \tau_B$ and $\tau = \tau_A \tau_B / (\tau_A + \tau_B) = \tau_A / 2$. In the slow exchange limit, the two methyl resonances have the same line width; hence $T_{2A} = T_{2B} = T_2$, where T_2 is the transverse relaxation time. For an exchange process of this type, the dependence of the nmr line shape on τ , T_2 , and $\delta\nu$, the frequency separation between the two resonances in absence of exchange, has been given by Gutowsky and Holm.³¹

Values of τ were obtained by comparing observed spectra in the coalescence region with line shapes computed for various values of τ , a fixed value of T_2 , and the measured value of $\delta\nu$. In general, at least five copies of each spectrum were recorded. The relaxation time was obtained from line-width measurements by a method which will be described later. Line shapes were computed for an appropriate range of *ca.* 40 values of τ . Observed and calculated spectra were compared with regard to (1) line widths at three-fourths, one-half, and one-fourth maximum amplitude (above the coalescence temperature) and (2) $\delta\nu_c$, the frequency separation between the two absorption maxima, and r , the

ratio of the maximum amplitude to the amplitude at $(\nu_A + \nu_B)/2$ (below the coalescence temperature). In some cases, a comparison of the full line shape was made. The more important features of the observed spectra are summarized in Tables III, IV, and V.

TABLE III

VARIABLE-TEMPERATURE NMR DATA FOR Ti(acac)₂F₂^a

Temp, °C	Line width, ^b cps	$\delta\nu_c$, cps	r
-47.5	1.26
-50.6	1.40
-52.5	1.61
-55.3	1.90
-58.5	2.45
-60.8	2.85
-62.8	3.38
-65.0	3.80	1.24	1.01
-68.0	...	2.04	1.20
-69.8	...	2.25	1.39
-73.5	...	2.37	1.44
-77.5	...	2.56	1.51
-84.5	...	2.46	1.51

$$\delta\nu_c = 2.56 \text{ cps; } T_c^d = -63^\circ$$

^a 0.316 *M* in dichloromethane. ^b Width of resonance line at half-maximum amplitude. ^c Frequency separation in the slow exchange limit. ^d Coalescence temperature.

TABLE IV

VARIABLE-TEMPERATURE NMR DATA FOR Ti(acac)₂Cl₂^a

Temp, °C	Line width, ^b cps	$\delta\nu_c$, cps	r
-11.8	1.98
-14.3	2.35
-16.0	2.51
-19.1	3.42
-20.4	4.43
-22.0	5.08
-23.5	5.86
-26.2	7.17	~1.7	<1.01
-27.5	7.70	~2.7	<1.02
-29.3	...	4.28	1.17
-31.4	...	5.30	1.63
-34.4	...	5.81	1.99
-36.9	3.12	6.01	2.42
-40.2	2.12	6.27	4.18
-50.5	1.62	6.39	7.72
-54.0	1.33	6.40	13.7
-63.5	1.43	6.38	12.9

$$\delta\nu_c = 6.40 \text{ cps; } T_c^d = -26^\circ$$

^a 0.315 *M* in dichloromethane. ^b Width of resonance line at half-maximum amplitude. ^c Frequency separation in the slow exchange limit. ^d Coalescence temperature.

In order to compute the line shape, the relaxation time T_2 is needed. Ordinarily, this quantity is obtained from line widths in the very slow or very fast exchange limits; in these limits, the line width at half-maximum amplitude in units of radians/sec is equal to $2/T_2$. For the Ti(acac)₂X₂ complexes, line widths increase from *ca.* 0.4 cps in the fast exchange limit (*ca.* +60°) to more than 1 cps in the slow exchange limit. In view of the strong temperature dependence of T_2 , the values of T_2 in the slow and fast exchange limits are not appropriate for calculation of line shapes in the coalescence region.

(31) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956). eq 4.

TABLE V

VARIABLE-TEMPERATURE NMR DATA FOR $\text{Ti}(\text{acac})_2\text{Br}_2^a$

Temp, °C	Line width, ^b cps	$\delta\nu^c$, cps	τ
-20.0	2.48
-24.0	3.28
-26.0	4.21
-28.8	6.04
-30.8	7.68
-33.0	8.99
-36.0	...	5.77	1.14
-39.6	...	7.55	1.75
-42.3	3.96	8.27	2.62
-44.5	3.21	8.49	3.71
-50.5	1.87	8.90	9.2
-54.0	1.72	9.08	23
-63.0	1.32	9.11	35

 $\delta\nu^c = 9.11$ cps; $T_c^d = -34^\circ$

^a 0.154 M in dichloromethane. ^b Width of resonance line at half-maximum amplitude. ^c Frequency separation in the slow exchange limit. ^d Coalescence temperature.

Values of T_2 in the coalescence region were estimated from line widths of the methyl resonance of the analogous zirconium complex, $\text{Zr}(\text{acac})_2\text{Cl}_2$. Chemical shift data suggest that this complex is a *cis* isomer; however, only one methyl signal is observed due to very rapid exchange of methyl groups.³² The exchange is sufficiently fast so that exchange effects do not alter the line shape in the temperature region of interest. Figure 4 shows the increase in line width with decreasing temperature for $\text{Zr}(\text{acac})_2\text{Cl}_2$. Rhodium(III) acetylacetonate, a symmetrical, kinetically inert chelate, exhibits nearly the same temperature dependence.

It was assumed that the curve in Figure 4 for $\text{Zr}(\text{acac})_2\text{Cl}_2$ gives the line widths which the $\text{Ti}(\text{acac})_2\text{X}_2$ complexes would have in the absence of exchange. For each $\text{Ti}(\text{acac})_2\text{X}_2$ complex, three values of T_2 were read off the curve at temperatures in the range where kinetic data were collected. The line-shape computations were carried through for all three values of T_2 in order to assess the effect of uncertainty in T_2 on the derived values of τ and associated activation parameters. For $\text{Ti}(\text{acac})_2\text{Cl}_2$, computations were also made using the value of T_2 obtained from the line width of $\text{Ti}(\text{acac})_2\text{Cl}_2$ in the fast exchange limit. By comparison of observed and computed spectra, values of τ were obtained for temperatures listed in Tables III, IV, and V. Lifetimes at a few selected temperatures and activation parameters are listed in Table VI. The activation energy, E_a , and frequency factor, A , for exchange of methyl groups were obtained from $\log k$ vs. $1/T$ plots, where $k = 1/2\tau$ is the first order rate constant for exchange. The activation entropy, ΔS^* , extrapolated to 25° , was calculated from the relation

$$\Delta S^* = R[\ln A - \ln(RT/Nh)] - R$$

where R , N , and h have their usual significance and temperature is taken to be 298°K . It can be seen from Table VI that an overestimate of T_2 decreases both E_a and ΔS^* . In the case of the dichloride and the dibromide, for reasonable estimates of T_2 , uncertainty in

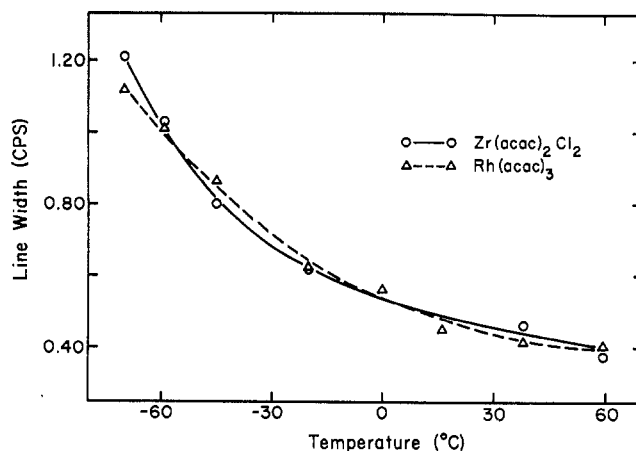


Figure 4. Temperature dependence of methyl line width at half-maximum amplitude [$1/(\pi T_2)$ cps] for $\text{Zr}(\text{acac})_2\text{Cl}_2$ and $\text{Rh}(\text{acac})_3$ in dichloromethane solution.

TABLE VI
EFFECT OF T_2 ON KINETIC DATA

T_2 , sec	Temp, °C ^a	Temp, °C ^b	$\tau \times 10^2$, sec	E_a , kcal/mole	ΔS^* , eu
$\text{Ti}(\text{acac})_2\text{F}_2$					
0.348	-53	-50.6	2.4	11.4 ± 0.6^c	-4 ± 3^e
		-62.8	11.5		
		-69.8	27		
0.316	-59	-50.6	2.0	12.4 ± 1.0	2 ± 5
		-62.8	11.0		
		-69.8	28		
0.280	-66	-50.6	1.4	15.2 ± 2.3	15 ± 11
		-62.8	10.4		
		-69.8	29		
$\text{Ti}(\text{acac})_2\text{Cl}_2$					
0.884 ^d		-14.3	1.41	9.8 ± 0.6^e	-16 ± 3^e
		-26.2	3.8		
		-36.9	8.2		
0.535	-15	-14.3	1.29	10.8 ± 0.7	-12 ± 3
		-26.2	3.9		
		-36.9	8.9		
0.487	-26	-14.3	1.25	11.1 ± 0.7	-10 ± 3
		-26.2	3.9		
		-36.9	9.1		
0.427	-38	-14.3	1.19	11.6 ± 0.7	-8 ± 3
		-26.2	3.9		
		-36.9	9.5		
$\text{Ti}(\text{acac})_2\text{Br}_2$					
0.500	-23	-24.0	0.96	11.3 ± 0.4	-7 ± 2
		-33.0	2.35		
		-42.3	6.3		
0.444	-34.5	-24.0	0.93	11.6 ± 0.5	-6 ± 2
		-33.0	2.34		
		-42.3	6.4		
0.374	-48	-24.0	0.89	12.1 ± 0.6	-4 ± 2
		-33.0	2.32		
		-42.3	6.5		

^a Temperature at which T_2 was estimated from Figure 4.^b Temperature at which spectrum was recorded. ^c Errors were estimated by least-squares analysis at the 95% confidence level.^d Obtained from the line width of $\text{Ti}(\text{acac})_2\text{Cl}_2$ in the fast exchange limit. ^e These values are in agreement with the results of Bradley and Holloway.²⁹

T_2 produces systematic errors in E_a and ΔS^* which are less than 0.8 kcal/mole and 4 eu, respectively. For the difluoride, which has a lower coalescence temperature

and much more closely spaced resonances in absence of exchange, the errors are considerably larger.

We wish to separate the temperature dependence of τ and T_2 so that systematic errors in τ owing to the temperature dependence of T_2 may be minimized. The following procedure was used in hopes of minimizing these errors: the observed spectrum at a given temperature was compared with the spectrum which had been calculated using a value of T_2 most appropriate for that temperature. For example, spectra were calculated for $\text{Ti}(\text{acac})_2\text{Cl}_2$ using values of T_2 which should be appropriate at temperatures of -15° , -26° , and -38° (cf. Table VI). Observed spectra (Table IV) in the range -11.8 to -19.1° were compared with spectra which had been calculated using the -15° value of T_2 . Spectra recorded at -20.4 to -31.4° and -34.4 to -40.2° were compared with calculated spectra based on the -26 and -38° values, respectively, of T_2 . Values of τ obtained by this treatment are presented in Table VII. Also included are values of E_a , $\log A$, and ΔS^* at 25° ; these parameters were obtained from the linear $\log k$ vs. $1/T$ plots of Figure 5.³³

The data of Table VII indicate that the $\text{Ti}(\text{acac})_2\text{X}_2$ complexes are quite labile with respect to changes in the configuration of the acetylacetonate rings. First-order rate constants for methyl group exchange, extrapolated to 25° , are $1.6 \times 10^4 \text{ sec}^{-1}$ ($\text{X} = \text{F}$), $6.7 \times 10^2 \text{ sec}^{-1}$ ($\text{X} = \text{Cl}$), and $2.3 \times 10^3 \text{ sec}^{-1}$ ($\text{X} = \text{Br}$). Even at -40° methyl groups "jump" from one site to the other at rates of 69, 3.4, and 9.9 times per second for $\text{X} = \text{F}$, Cl , and Br , respectively. The activation energies appear to be identical within experimental error. Increasing lability in the order $\text{X} = \text{F} > \text{Br} > \text{Cl}$ must be attributed to differences in the entropies of activation. The differences in ΔS^* appear to be statistically significant, at least for $\text{X} = \text{Cl}$ and Br . In the case of $\text{Ti}(\text{acac})_2\text{F}_2$ estimates of error in the activation parameters should probably be considerably larger than the estimates of Table VII because of the strong dependence of E_a and ΔS^* on the choice of T_2 (cf. Table VI).

Sufficient experimental data are not yet available to permit a definitive statement on the mechanism of these stereochemical rearrangements. However, it will be useful to comment briefly on some of the possibilities. In calculations of rate constants and entropies of activation, we have assumed that exchange of methyl groups is a first-order process. The rather unlikely possibility of exchange requiring a bimolecular collision of $\text{Ti}(\text{acac})_2\text{X}_2$ molecules was eliminated by measuring values of τ at two different concentrations. For a second-order process τ should be inversely proportional to the $\text{Ti}(\text{acac})_2\text{X}_2$ concentration. The data pre-

(33) Independent kinetic runs indicated that the reproducibility of the τ values is ca. $\pm 10\%$. Errors in τ due to errors in measurement of line widths and line separations amount to only 2-3%. A more serious source of error is the control and measurement of temperature. Scatter in the data of Figure 5 ($\pm 6\%$ in τ) can be accounted for by temperature errors of ca. $\pm 0.6^\circ$. The possible presence of traces of water does not appear to be a significant source of error; line shapes of the methyl resonances of $\text{Ti}(\text{acac})_2\text{Cl}_2$ at -19.5 , -24.5 , and -37.0° are the same for (a) 0.315 M $\text{Ti}(\text{acac})_2\text{Cl}_2$ in dry dichloromethane and (b) 0.315 M $\text{Ti}(\text{acac})_2\text{Cl}_2$ in dichloromethane which had been saturated with water at 25° .

TABLE VII
KINETIC DATA FOR METHYL GROUP EXCHANGE^a

$\text{Ti}(\text{acac})_2\text{F}_2$		$\text{Ti}(\text{acac})_2\text{Cl}_2$		$\text{Ti}(\text{acac})_2\text{Br}_2$	
Temp, $^\circ\text{C}$	$\tau \times 10^2$, sec	Temp, $^\circ\text{C}$	$\tau \times 10^2$, sec	Temp, $^\circ\text{C}$	$\tau \times 10^2$, sec
-47.5	1.6	-11.8	1.1	-20.0	0.69
-50.6	2.4	-14.3	1.3	-24.0	0.96
-52.5	3.3	-16.0	1.4	-26.0	1.3
-55.3	4.4	-19.1	1.9	-28.8	1.7
-58.5	6.4	-20.4	2.5	-30.8	2.0
-60.8	8.1	-22.0	2.8	-33.0	2.3
-62.8	10.7	-23.5	3.1	-36.0	3.3
-65.0	14	-26.2	3.9	-39.6	4.7
-68.0	22	-27.5	4.2	-42.3	6.4
-69.8	29	-29.3	5.0	-44.5	8.2
		-31.4	6.9		
		-34.4	8.3		
		-36.9	9.5		
		-40.2	15		
E_a , kcal/mole	11.6 ± 0.5^b	11.2 ± 0.6	11.6 ± 0.4		
$\log A$	12.70 ± 0.49	11.03 ± 0.51	11.85 ± 0.36		
ΔS^* , eu	-2.4 ± 2.3	-10.0 ± 2.3	-6.3 ± 1.6		

^a In dichloromethane solution; corrected for the temperature dependence of T_2 . ^b Estimates of error (95% confidence level) reflect scatter in the data of Figure 5 but do not include any remaining systematic errors due to the temperature variation of T_2 .

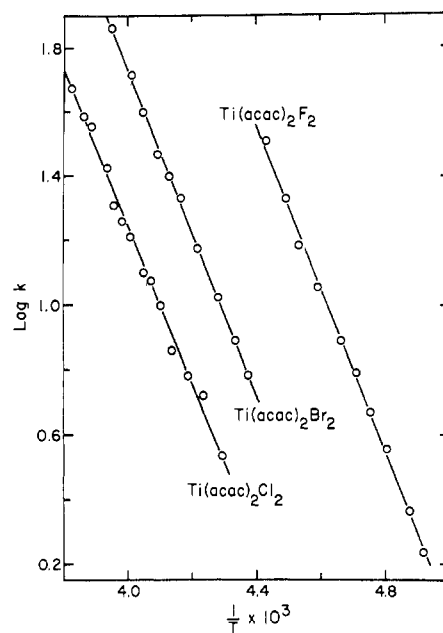


Figure 5.— $\log k$ vs. $1/T$ plots for $\text{Ti}(\text{acac})_2\text{X}_2$ complexes; $k = 1/2\tau$ is the first-order rate constant for exchange of methyl groups.

sented in Table VIII indicate that τ is independent of concentration, as expected for a first-order reaction. The following first-order processes could interchange methyl groups between the two environments: (1) dissociation of a halide ion to give a five-coordinate intermediate; (2) rupture of one M-O bond to give a five-coordinate intermediate which has one monodentate acetylacetonate ligand; (3) complete dissociation of one acetylacetonate ligand; and (4) twist mechanisms which exchange methyl groups without metal-ligand bond rupture.

Halide dissociation is not an attractive mechanism because (a) the activation energies are independent of

TABLE VIII
CONCENTRATION DEPENDENCE OF LIFETIMES
FOR METHYL GROUP EXCHANGE^a

Temp, °C	Ti(acac) ₂ F ₂	
	0.163 M τ × 10 ² , sec	0.316 M τ × 10 ² , sec
-59.1	8.3	7.8
-63.0	14	15
-67.1	21	19
Temp, °C	Ti(acac) ₂ Cl ₂	
	0.173 M τ × 10 ² , sec	0.315 M τ × 10 ² , sec
-20.7	2.3	2.4
-24.7	3.6	3.6
-30.7	5.5	5.4
Temp, °C	Ti(acac) ₂ Br ₂	
	0.088 M τ × 10 ² , sec	0.154 M τ × 10 ² , sec
-20.7	0.88	0.89
-31.0	2.3	2.3
-39.4	4.4	4.7

^a In dichloromethane solution.

the halogen and (b) the dialkoxides, Ti(acac)₂(OR)₂, also exhibit methyl group exchange with activation energies very similar to those for the dihalides.²⁹ It is likely that there is some halide dissociation in dichloromethane since halide ligand exchange reactions occur; for example, Ti(acac)₂F₂ and Ti(acac)₂Br₂ give an equilibrium mixture of starting materials plus the mixed complex, Ti(acac)₂FBr. However, nmr spectra indicate that the rate of halide exchange is slow compared with the rate of exchange of methyl groups. There-

fore, complete dissociation of halide ligands cannot be the mechanism for methyl group exchange.

Complete dissociation of an acetylacetonate ligand requires rupture of two M-O bonds. This mechanism, which seems less likely than the one-bond rupture mechanism, may be eliminated since exchange of acetylacetonate ligands with excess acetylacetone is not observed under conditions where exchange of Ti(acac)₂X₂ methyl groups is fast. At 37° dichloromethane solutions containing Ti(acac)₂X₂ and H(acac) (1:2 mole ratio) give two methyl resonances separated by 4 to 8 cps. The line width of the Ti(acac)₂X₂ resonance is the same as in the absence of excess H(acac). Dissociation of bidentate ligands has also been excluded in the case of Sn(acac)₂Cl₂, where tin-ring proton spin coupling is observed before, during, and after coalescence of the methyl resonances.³⁰

Variable-temperature nmr studies of the bis-benzoyl-acetonato complexes, Ti(bzac)₂X₂, allow elimination of certain twisting mechanisms.³⁴ It appears that rupture of one M-O bond may be the preferred mechanism for these stereochemical rearrangements. We are continuing experiments designed to provide further evidence on this point.

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(34) N. Serpone and R. C. Fay, *Inorg. Chem.*, in press.

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The Use of Chromium(IV) Diperoxo Amines in the Synthesis of Chromium(III) Amine Complexes. III. Some Bromo, Phosphato, and Sulfato Ethylenediamine Complexes¹

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Treatment of [Cr(en)(OH₂)(O₂)₂]·H₂O with 7 F HBr gave the new greenish purple compound [Cr(en)(OH₂)₂Br₂]Br in ca. 90% purity. Cation-exchange chromatography of a 0.01 F HClO₄ solution of the solid resulted in isolation of the new green-blue complex Cr(en)(OH₂)₂Br₂⁺, together with low yields of Cr(en)(OH₂)₄³⁺ and a green polymer. Hydrolysis of green-blue Cr(en)(OH₂)₂Br₂⁺ yielded the new magenta complex Cr(en)(OH₂)₃Br²⁺. The action of 5 F H₃PO₄ on [Cr(en)(OH₂)(O₂)₂]·H₂O gave a solution from which the new pink complex Cr(en)(OH₂)₃HPO₄⁺ (or possibly Cr(en)(OH₂)₂HPO₄⁺) was isolated chromatographically; species which may be Cr(en)(OH)₃PO₄ and Cr(en)(OH₂)₃H₂PO₄²⁺ were also produced. Dissolution of [Cr(en)(OH₂)(O₂)₂]·H₂O in 6 F H₂SO₄ gave a solution from which the new pink complex Cr(en)(OH₂)₃SO₄⁺ (or possibly Cr(en)(OH₂)₂SO₄⁺) was chromatographically isolated. No evidence of any nitrate complexes was found on treatment of [Cr(en)(OH₂)(O₂)₂]·H₂O with 7 F HNO₃, only Cr(en)(OH₂)₄³⁺ being formed. The geometric configurations of these new diaquo and triaquo complexes are unknown. Maxima and minima of the visible absorption spectra of the new complexes are presented.

Introduction

The previous papers of this series^{2,3} described the synthesis of some chromium(IV) diperoxo amines and

their use in the preparation of some ethylenediamine, ammineethylenediamine, propylenediamine, isobutylene-

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