an Fe-N bond breaks it results in dissociation. Hence, the ratio $k_0/k_{01} = k_{03}/(k_{02} + k_{03}) = 0.422$ is the probability of the occurrence of the acid-independent dissociation.

The activation energy for the dissociation of DB in 0.03 *M* nitric acid is 14 ± 2 kcal. It is to be noted that this activation energy, since it is obtained at low acid concentration, is a measure of the activation energy indicated with the rate constant $k_{01}k_{03}/(k_{02} + k_{03})$.

Dissociation of the Phenanthroline Complex (DP). As in the case of the bipyridine complex, the binuclear phenanthroline complex $[(\text{phen})_2(H_2O)\text{Fe-O-Fe}(H_2O)(\text{phen})_2]^{4+}$ dissociates in dilute nitric acid with complete loss of color. The dissociation exhibits a first-order dependence on the complex concentration. No intermediate or isosbestic point was observed. But in comparison to DB, DP shows a relatively smaller dependence on the acid concentration (Figure 1).
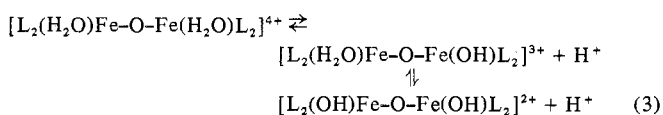
Because of the rigidity of the phenanthroline rings, half-bonded structures similar to that of III (Scheme II) are not possible. When one Fe-N bond is broken, either reclosure occurs or the second Fe-N bond also breaks off effecting complete dissociation of the phen molecule. Hence, the acid-dependent part of the dissociation depicted in Scheme II (corresponding to k_{04}) is not possible for DP. The dissociation of DP may be described by two parallel reactions: (i) the acid-dependent reaction identical to Scheme I and (ii) the simple dissociation or acid-independent pathway similar to the ones indicated by the rates k_{01}, k_{02}, and k_{03} in Scheme II. Hence, the observed rate constant for the dissociation of DP is

$$k_{\text{obsd}} = \frac{k_{01}k_{03}}{k_{02} + k_{03}} + K_{\text{eq}}k_1[\text{H}^+] \tag{2}$$

At nitric acid concentrations greater than 0.4 *M*, where a limiting rate is reached, the observed rate constant $k_\infty = k_{01}k_{03}/(k_{02} + k_{03}) + k_1$ and is equal to 1.66×10^{-3} sec^{-1} at 23°. The intercept of the plot of k_{obsd} vs. $[\text{H}^+]$ gives k_0 and is equal to 0.90×10^{-3} sec^{-1} at 23° (Figure 1).[12] Hence, the difference between k_∞ and k_0 is k_1, which is the acid-dependent rate constant (*cf.* Scheme I) for the dissociation of DP, and is equal to 0.76×10^{-3} sec^{-1} at 23°. The slope of the plot of k_{obsd} vs. $[\text{H}^+]$ is equal to $K_{\text{eq}}k_1 = 2.73 \times 10^{-3}$. Since $k_1 = 0.76 \times 10^{-3}$ sec^{-1}, we calculate $K_{\text{eq}} = 3.60$.

The activation energy for the dissociation of DP in 0.03 *M* nitric acid is 16 ± 2 kcal. Within experimental uncertainty, this value is comparable to that for the dissociation of DB. As pointed out in the case of DB, the activation energy for the dissociation of DP is for the rate constant indicated by $k_{01}k_{03}/(k_{02} + k_{03})$.

There is no spectral evidence for the formation of the O-protonated species $[L_2(H_2O)\text{Fe-OH-Fe}(H_2O)L_2]^{5+}$ in aqueous acid solutions (*cf.* Scheme I). But this is not surprising if we observe that DP and DB behave as acids in aqueous media (a 2.5×10^{-4} *M* solution of the complex has a pH of 4.0). This acidic behavior has been attributed to the presence of the equilibrium[7]

$$[L_2(H_2O)\text{Fe-O-Fe}(H_2O)L_2]^{4+} \rightleftarrows$$
$$[L_2(H_2O)\text{Fe-O-Fe}(OH)L_2]^{3+} + \text{H}^+$$
$$\updownarrow$$
$$[L_2(OH)\text{Fe-O-Fe}(OH)L_2]^{2+} + \text{H}^+ \tag{3}$$

But, in addition to the above equilibrium, the presence of an equilibrium of the following type cannot be ruled out

$$[L_2(H_2O)\text{Fe-O-Fe}(H_2O)L_2]^{4+} \rightleftarrows [L_2(OH)\text{Fe-OH-Fe}(H_2O)L_2]^{4+} \tag{4}$$
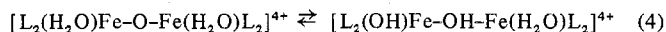
It is reasonable to believe that the difference between the absorption maxima of the charge-transfer bands of the O-protonated and unprotonated species will not be more than 5-10 nm and, hence, the electronic absorption spectrum of even an aqueous solution of DB or DP may be an additive superimposition of the spectra due to the O-protonated and unprotonated species. Hence, definitive spectral evidence for the protonated species may not be obtained. Furthermore, it is not unlikely that the O-protonated and unprotonated species have essentially identical electron spectra.

An indirect evidence for the formation of the O-protonated species comes from the reactions of DB and DP with potassium thiocyanate.[9] Addition of potassium thiocyanate to an acidic aqueous solution (pH 1.3) of DP or DB results in the immediate precipitation of $[\text{FeL}_2(\text{NCS})_2]^+$, while a mixture of $[\text{FeL}_2(\text{NCS})_2]^+$ and $[L_2(\text{NCS})\text{Fe-O-Fe}(\text{NCS})L_2]^{2+}$ precipitates out in the intermediate pH ranges 1.3-4.0. At high acid concentrations only the O-protonated species exists; protonation at the "bridge" oxygen weakens the Fe-O-Fe bonds, thus accelerating its cleavage. At low acid concentration, where a mixture of $[L_2(H_2O)\text{Fe-O-Fe}(H_2O)L_2]^{4+}$ and $[L_2(H_2O)\text{Fe-OH-Fe}(H_2O)L_2]^{5+}$ exists in solution, reaction with NCS$^-$ results in a mixture of $[\text{FeL}_2(\text{NCS})_2]^+$ and $[L_2(\text{NCS})\text{Fe-O-Fe}(\text{NCS})L_2]^{2+}$.

The reactions of DP and DB with potassium thiocyanate[9] can further be taken as an indirect proof for the occurrence of the dissociation pathway depicted in Scheme I. Formation of $[\text{FeL}_2(\text{NCS})]^+$ cannot be explained if Scheme II is the only one responsible for the dissociation reactions of DP and DB. Isolation of $\text{FeL}_2(\text{NCS})_2^+$ may be taken as a conclusive evidence for the formation of $[\text{FeL}_2(H_2O)]^{3+}$ as a transient species (Scheme I) during the acid dissociation reactions.

Contribution from the Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185

Preparation and Characterization of Chloro(alkoxy)bis(2,4-pentanedionato)titanium(IV) Complexes

D. W. Thompson,* W. R. C. Munsey, and Thomas V. Harris

During the past few years several studies have been reported concerning the synthesis and characterization of hexacoordinate titanium(IV) complexes comprised of two oxygen-chelated 2,4-pentanedionate groups and two monodentate ligands. The most thoroughly studied of these complexes have been the dialkoxy-[1] and dihalobis(2,4-pentanedionato)titanium(IV)[2] complexes. One of the most intriguing

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(12) The difference between the values of the intercept (0.90×10^{-3}) and the k_{obsd} at 0.03 *M* nitric acid (0.92×10^{-3}) is negligible, and, hence, for all practical purposes they may be taken to be the same.

(1) J. F. Harrod and K. Taylor, *Chem. Commun.*, 696 (1971), and references cited therein.

(2) R. C. Fay and R. N. Lowry, *Inorg. Chem.*, 9, 2048 (1970), and references cited therein.

Table I

| Complex | Calcd, % | | | Found, % | | | Mp, °C dec | Molar conductance, $\Lambda_M{}^a$ cm² mol⁻¹ ohm⁻¹ |
	C	H	Cl	C	H	X[c]		
Cl(CH₃O)Ti(C₅H₇O₂)₂	42.26	5.48	11.34	42.11	5.51	12.43	105–109	0.48 (5.8 × 10⁻³ *M*)
Cl(C₂H₅O)Ti(C₅H₇O₂)₂	44.12	5.87	10.85	43.83	5.64	12.19	91–95	0.42 (5.8 × 10⁻³ *M*)
Cl(*n*-C₃H₇O)Ti(C₅H₇O₂)₂	45.84	6.21	10.41	45.61	6.08	10.80	84–88	0.31 (3.0 × 10⁻³ *M*)
Cl(*i*-C₃H₇O)Ti(C₅H₇O₂)₂	45.84	6.21	10.41	45.76	6.23	10.90	110–104	0.55 (5.3 × 10⁻³ *M*)
Cl(C₃H₅O)Ti(C₅H₇O₂)₂	46.11	5.66	10.47	46.09	5.72	11.13	119–122	0.26 (3.7 × 10⁻³ *M*)
(C₅H₅NH)₂[(CH₃O)TiCl₅]	31.72	3.63	42.56	31.74	3.91	42.21	175	*b*
(C₅H₅NH)₂[(C₂H₅O)TiCl₅]	33.48	3.98	41.18	33.13	4.17	40.51	195	*b*
(C₅H₅NH)₂[(*n*-C₃H₇O)TiCl₅]	35.13	4.31	39.88	35.09	4.50	39.24	215	*b*
(C₅H₅NH)₂[(*i*-C₃H₇O)TiCl₅]	35.13	4.31	39.88	34.87	4.20	39.47	210	*b*
(C₅H₅NH)₂[(C₃H₅O)TiCl₅]	35.29	3.87	40.06	34.93	4.04	39.51	185	*b*

a Solvent is nitrobenzene. Concentration values are in parentheses. *b* Limited solubility precluded conductivity measurements. *c* Halogen analyses are consistently high and suggest that the halogen-rich pyridinium alkoxypentahalogenotitanate salt may yet be a minor impurity making the apparent melting points too low.

features of these complexes is the preponderance of the cis (C_2) stereochemistry. We wish to report on the preparation and structure of several mixed chloro(alkoxy)bis(2,4-pentanedionato)titanium(IV) complexes.

Experimental Section

Reagents. Pyridine and the alcohols were obtained from commercial sources and were distilled from suitable dehydrating agents and stored over appropriate molecular sieves before use.[3] 2,4-Pentanedione (Eastman Organic Chemicals) was distilled prior to use. Titanium tetrachloride (Fisher Scientific Co.) was used without further purification. Trichloro(2,4-pentanedionato)titanium(IV) was prepared by direct reaction of TiCl₄ and 2,4-pentanedione as reported by Puri and Mehrotra.[4] All solvents were purified by distillation under nitrogen or vacuum from suitable dehydrating agents before use. Nitrobenzene was purified in a manner similar to that reported.[5]

General Preparative Procedure for the Title Complexes. All complexes reported in Table I were prepared in a similar manner. All preparations were performed under an atmosphere of dry nitrogen. Solid materials were handled in a Vacuum/Atmospheres Dri-Lab glove box. Trichloro(2,4-pentanedionato)titanium(IV) was suspended in *ca.* 50 ml of methylene chloride. Pyridine and the appropriate alcohol were dissolved together in *ca.* 20 ml of methylene chloride; the resulting solution was added dropwise to the β-diketonate complex. For all preparations the mole ratios of the β-diketonate complex to pyridine to alcohol were 1:1:1. During the course of the addition the solid in the reaction flask gradually turned from the deep red of the β-diketonate complex to a yellow-orange solid. Stirring was continued at room temperature for 0.5 hr. The solid was then filtered, washed with methylene chloride, and dried under vacuum at room temperature. Data for these initial products, which were found to be pyridinium pentachloroalkoxytitanate(IV) salts, are presented in Table I.

The filtrates from above were reduced to a small volume under vacuum at room temperature. Addition of hexane then caused the precipitation of yellow solids which were shown to be primarily the chloro(alkoxy)bis(2,4-pentanedionato)titanium(IV) complexes. However, in every case the products were contaminated with the pyridinium salt. Thus, all of these products were recrystallized from benzene which gave satisfactory complexes. Data for the chloro-(alkoxy)bis(2,4-pentanedionato)titanium(IV) complexes are presented in Table I.

Reaction of Dichlorobis(2,4-pentanedionato)titanium(IV) with Allyl Alcohol in the Presence of Pyridine. Dichlorobis(2,4-pentanedionato)titanium(IV) (4.8 × 10⁻² mol), synthesized by the method reported by Fay and Lowry,[5] was dissolved in 40 ml of methylene chloride. Allyl alcohol (5.1 × 10⁻² mol) and pyridine (5.1 × 10⁻² mol) dissolved in 20 ml of methylene chloride were added dropwise at 0° during which time a solid product formed. After complete addition the reaction mixture was stirred at room temperature for *ca.* 0.5 hr. The solid was isolated. Ir, mp (139–145°), and analytical

data were consistent with this product being pyridinium chloride.

An equal volume of hexane was added to the filtrate from above whereupon additional pyridinium chloride precipitated and was filtered off. Methylene chloride was removed under vacuum at room temperature from the second filtrate whereupon a yellow solid formed. This solid was isolated and recrystallized from benzene. Spectral properties and elemental analysis indicated that the complex was identical with the chloro(allyloxy)bis(2,4-pentanedionato)-titanium(IV) prepared above.

Conductance Measurements. These measurements were carried out as previously described.[6]

Melting Points. Melting points were measured in sealed capillaries with a Thomas-Hoover apparatus and are uncorrected.

Spectral Data. Proton nmr spectra were run on a Perkin-Elmer R-20B spectrometer. Infrared spectra were taken with a Perkin-Elmer 457 spectrophotometer.

Results and Discussion

The intent of our investigation was to study the reaction of simple alcohols with trichloro(2,4-pentanedionato)titanium-(IV), $Cl_3Ti(C_5H_7O_2)$. Since 2,4-pentanedione, a β-unsaturated alcohol, reacts with $Cl_3Ti(C_5H_7O_2)$ to give dichlorobis-(2,4-pentanedionato)titanium(IV), it was hypothesized that $Cl_3Ti(C_5H_7O_2)$ would react with simple alcohols to yield dichloroalkoxy(2,4-pentanedionato)titanium(IV) complexes. These complexes were of interest structurally with respect to the possibility of dimerization *via* alkoxy or chloride bridges. It was found, however, that direct reaction of $Cl_3Ti(C_5H_7O_2)$ with alcohols in refluxing methylene chloride led only to the isolation of the well-characterized $Cl_2Ti(C_5H_7O_2)_2$; no evidence for a $Cl_2(RO)Ti(C_5H_7O_2)$ species was obtained. It is unclear as to the route by which $Cl_2Ti(C_5H_7O_2)_2$ is formed. One plausible reaction scheme is displayed in eq 1. It may

$$Cl_3Ti(C_5H_7O_2) + ROH \rightarrow Cl_2(RO)TiL + HCl \rightarrow$$
$$\tfrac{1}{2}Cl_2TiL_2 + \tfrac{1}{2}Ti(RO)_2Cl_2 \qquad (1)$$
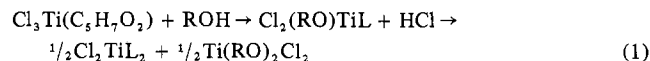
be that $Cl_3Ti(C_5H_7O_2)$ initially reacts with the alcohol to give the desired dichloroalkoxy species which then undergoes disproportionation to give the disubstituted product, Cl_2TiL_2, plus dialkoxydichlorotitanium(IV) compounds which are well known. No attempt was made to isolate these latter compounds. The disproportionation of $X_3Ti(C_5H_7O_2)$, X = OR or Cl, species to give $X_2Ti(C_5H_7O_2)_2$ complexes plus TiX₄ has been established.[7,8] Another plausible reaction pathway involves partial initial disproportionation of the Cl_3TiL complex to Cl_2TiL_2 and TiCl₄. The addition of alcohol to the

(3) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967.

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

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

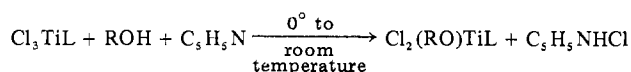(6) D. W. Thompson, J. F. Lefelhocz, and K. S. Wong, *Inorg. Chem.,* 11, 1139 (1972).

(7) D. W. Thompson, R. W. Rosser, and P. B. Barrett, *Inorg. Nucl. Chem. Lett.,* 7, 931 (1971).

(8) C. E. Holloway and A. E. Sentek, *Can. J. Chem.,* 49, 519 (1971).

system may push the disproportionation to the right by initially stabilizing the $TiCl_4$ as an alcohol adduct which then decomposes to $Ti(RO)_2Cl_2$ and HCl. The pathway is illustrated in eq 2.

$$2Cl_3TiL + 2ROH \rightarrow Cl_2TiL_2 + TiCl_4 \cdot 2ROH \rightarrow$$
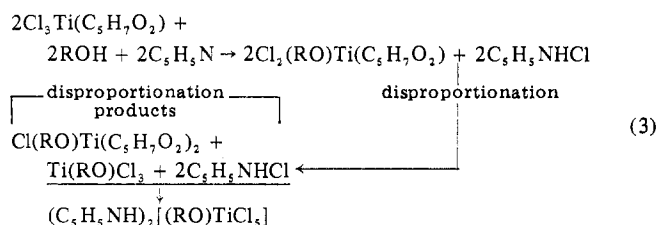$$Cl_2TiL_2 + Ti(RO)_2Cl_2 + 2HCl \qquad (2)$$
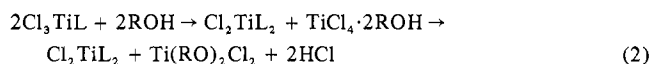
Being unsuccessful in preparing dichloro(alkoxy)(β-diketonate)titanium(IV) complexes by direct interaction of Cl_3TiL and alcohols, it was decided to include pyridine in the system to facilitate removal of HCl under mild conditions, *i.e.*

$$Cl_3TiL + ROH + C_5H_5N \xrightarrow[\substack{\text{room} \\ \text{temperature}}]{0^\circ \text{ to}} Cl_2(RO)TiL + C_5H_5NHCl$$

It was from these reactions that we isolated the previously unreported title complexes, chloro(alkoxy)bis(2,4-pentanedionato)titanium(IV) and pyridinium alkoxypentachlorotitanate(IV) salts. Conductivity, ir, and nmr data are consistent with the title complexes being neutral, monomeric, and hexacoordinate species.

A plausible pathway by which the $Cl(RO)Ti(C_5H_7O_2)_2$ complexes are formed is illustrated in eq 3. The alcohol may

$$2Cl_3Ti(C_5H_7O_2) +$$
$$2ROH + 2C_5H_5N \rightarrow 2Cl_2(RO)Ti(C_5H_7O_2) + 2C_5H_5NHCl$$

```
 ┌──disproportionation──┐      disproportionation
 │       products       │              │
Cl(RO)Ti(C5H7O2)2 +                    │                    (3)
   Ti(RO)Cl3 + 2C5H5NHCl ◄─────────────┘
        │
 (C5H5NH)2[(RO)TiCl5]
```

indeed react with $Cl_3Ti(C_5H_7O_2)$ in the presence of pyridine to form the initially desired $Cl_2(RO)Ti(C_5H_7O_2)$ complex and C_5H_5NHCl. The $Cl_2(RO)Ti(C_5H_7O_2)$ then undergoes disproportionation to ultimately yield $Cl(RO)Ti(C_5H_7O_2)_2$ and $(C_5H_6N)_2[(RO)TiCl_5]$. On the other hand, it is conceivable that the alcohol reacts with $Cl_2Ti(C_5H_7O_2)_2$ formed by initial disproportionation of $Cl_3Ti(C_5H_7O_2)$. This reaction pathway is illustrated in eq 4. The plausibility of this

$$2Cl_3Ti(C_5H_7O_2) \rightleftharpoons Cl_2Ti(C_5H_7O_2)_2 + TiCl_4$$
$$\downarrow \substack{2ROH \\ + \\ 2C_5H_5N} \qquad (4)$$
$$Cl(RO)Ti(C_5H_7O_2)_2 + C_5H_5NHCl + ROH + C_5H_5N + TiCl_4$$
$$\downarrow$$
$$(C_5H_5NH)_2[(RO)TiCl_5]$$
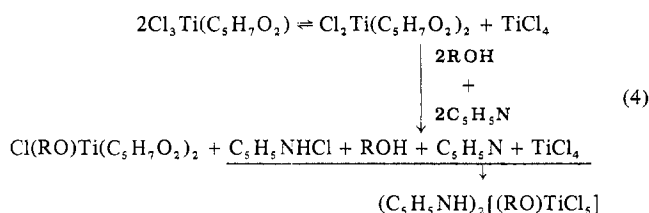
latter pathway is supported by the fact that we found that $Cl_2Ti(C_5H_7O_2)_2$ does react with alcohols in the presence of pyridine to give $Cl(RO)Ti(C_5H_7O_2)_2$ and C_5H_5NHCl. (See Experimental Section for a representative reaction with allyl alcohol.)

Since the cis stereochemistry is the dominant structural feature of the dihalo- and dialkoxybis(2,4-pentanedionato)titanium(IV) complexes, it was of interest to determine the stereochemistry of the mixed chloroalkoxy complexes. The cis configuration for all the title complexes is asymmetric and therefore under conditions of slow exchange should display in the proton nmr spectra four 2,4-pentanedionate methyl resonance peaks and two ring-proton peaks. At room temperature only a single methyl peak and a single ring peak were observed. Room temperature chemical shifts are

Complex	$-CH_3$	$=CH-$	$-CH_3$(alkoxide)
$Cl(CH_3O)Ti(C_5H_7O_2)_2$	-2.08	-5.71	-4.48 (s)
$Cl(C_2H_5O)Ti(C_5H_7O_2)_2$	-2.07	-5.70	-1.34 (t, $J = 6.7$ Hz)
$Cl(n\text{-}C_3H_7O)Ti(C_5H_7O_2)_2$	-2.03	-5.68	-0.95 (t, $J = 6.7$ Hz)
$Cl(i\text{-}C_3H_7O)Ti(C_5H_7O_2)_2$	-2.03	-5.67	-1.33 (d, $J = 6.4$ Hz)
$Cl(C_3H_5O)Ti(C_5H_7O_2)_2$	-2.06	-5.73	b

[a] Chemical shifts are in ppm relative to internal TMS. Concentrations are *ca.* 0.1 *M*. Further details of the spectra will be available on request. b A complex pattern for the propenoxy group is observed in the region -4.5 to -5.5.
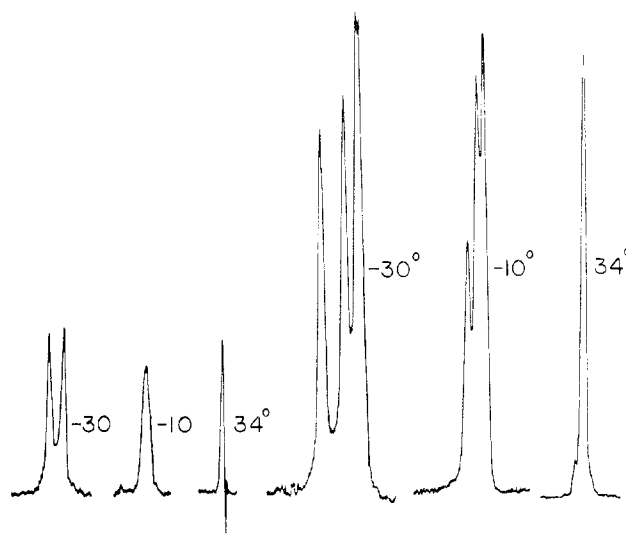

Figure 1. The nmr spectrum at various temperatures of the 2,4-pentanedionate protons in chloro(methoxy)bis(2,4-pentanedionato)titanium(IV) in chloroform (ethanol free). Spectrum amplitude varies.

recorded in Table II and are intermediate between those observed for the dihalo- and dialkoxybis(2,4-pentanedionato)titanium(IV) complexes.[5,9] However, at lower temperatures the ring-proton peak splits into two peaks of apparent equal intensity and the methyl region splits into three peaks with an intensity ratio of *ca.* 1:1:2. These splittings and relative intensities indicate that the cis isomers predominate at least in chloroform solution, the methyl patterns being only partially resolved due to accidental degeneracy. The low-temperature spectrum of chloro(methoxy)bis(2,4-pentanedionato)titanium(IV) is displayed in Figure 1. This spectrum is representative of that obtained for the remaining four analogous complexes with the exception that in this one case the third methyl peak is just resolved so that all four methyl peaks are observed.

(9) D. C. Bradley and C. E. Holloway, *J. Chem. Soc. A*, 282 (1969).