

from the aryl ring when the thiol proton is replaced by a carbene carbon atom.

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## Dipseudohalobis( $\beta$ -diketonato)titanium(IV) Complexes. Synthesis, Stereochemistry, Configurational Rearrangements, and Vibrational Spectra

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Dipseudohalobis( $\beta$ -diketonato)titanium(IV) complexes of the type  $\text{Ti}(\text{dik})_2(\text{NCO})_2$  and  $\text{Ti}(\text{dik})_2(\text{NCS})_2$ , where  $\text{dik} = \text{CH}_3\text{COCHCOCH}_3$  (acac) or *tert*- $\text{C}_4\text{H}_9\text{COCHCO-tert-C}_4\text{H}_9$  (dpm), have been prepared by reaction of  $\text{Ti}(\text{dik})_2\text{Cl}_2$  with  $\text{AgNCO}$  or  $\text{NaSCN}$ . Molecular weight, conductance, dipole moment, and nmr data demonstrate that these complexes and the previously unreported dichloro complex  $\text{Ti}(\text{dpm})_2\text{Cl}_2$  are monomeric nonelectrolytes which exist in solution as *cis* geometrical isomers. Variable-temperature nmr spectra show that the  $\beta$ -diketonate rings undergo rapid intramolecular configurational rearrangement which exchanges acac methyl groups (or dpm *tert*-butyl groups) between the two nonequivalent sites of the *cis* isomer. First-order rate constants ( $\text{sec}^{-1}$ ), extrapolated to 25°, activation energies (kcal/mol), and activation entropies (eu) in dichloromethane solution are respectively as follows:  $1.1 \times 10^3$ ,  $11.0 \pm 0.6$ ,  $-9.3 \pm 2.4$  for  $\text{Ti}(\text{acac})_2(\text{NCO})_2$ ;  $6.7 \times 10^3$ ,  $9.8 \pm 0.3$ ,  $-9.5 \pm 1.5$  for  $\text{Ti}(\text{dpm})_2(\text{NCO})_2$ ;  $3.5 \times 10^3$ ,  $11.4 \pm 0.4$ ,  $-5.6 \pm 1.5$  for  $\text{Ti}(\text{dpm})_2\text{Cl}_2$ . The  $\text{Ti}(\text{dik})_2(\text{NCS})_2$  complexes rearrange faster (by a factor of  $\sim 10^2$ ) than the  $\text{Ti}(\text{dik})_2(\text{NCO})_2$  analogs, but precise kinetic data could not be obtained because of the low coalescence temperatures. Infrared frequencies are reported in the range 2300–300  $\text{cm}^{-1}$ ; band assignments are given. The spectra point to an N-bonded attachment of the pseudohalide ligands and indicate that the complexes exist as the *cis* isomer in the solid state as well as in solution.

### Introduction

Previous papers from this laboratory have described the synthesis, stereochemistry, and configurational rearrangements of dihalobis( $\beta$ -diketonato)titanium(IV) complexes,  $\text{Ti}(\text{dik})_2\text{X}_2$ .<sup>1–4</sup> The difluoro, dichloro, and dibromo complexes exist in solution as stereochemically nonrigid *cis* octahedral isomers,<sup>1–3</sup> while the diiodo complex,  $\text{Ti}(\text{acac})_2\text{I}_2$ ,<sup>5</sup> is present in dichloromethane as an equilibrium mixture of rapidly isomerizing *cis* and *trans* isomers.<sup>4</sup> Reported herein are the results of related studies of new dipseudohalo analogs of the type  $\text{Ti}(\text{dik})_2(\text{NCO})_2$  and  $\text{Ti}(\text{dik})_2(\text{NCS})_2$  ( $\text{dik} = \text{acac}$  or  $\text{dpm}$ ).<sup>5</sup>

### Experimental Section

**Reagents and General Techniques.** Acetylacetone, bp 136–140°, and titanium tetrachloride (Matheson Coleman and Bell) were used as purchased without further purification. Dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione) was prepared by the method of

Man, *et al.*,<sup>6</sup> and purified by conversion to the copper chelate. Sodium thiocyanate was dried *in vacuo* at 175° for 48 hr, with periodic grinding in a mortar during the drying. Silver cyanate was prepared in aqueous solution by reaction of potassium cyanate and silver nitrate. The product was washed with acetone and dried *in vacuo* at room temperature for 48 hr in the dark. Reaction mixtures containing this compound were well shielded from direct light. Solvents (benzene, hexane, dichloromethane, and deuteriochloroform) were dried by refluxing for at least 24 hr over calcium hydride. Nitrobenzene was purified for conductance measurements by a previously described method;<sup>1</sup> the specific conductance of the purified solvent was  $< 4 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ . Because the  $\text{Ti}(\text{dik})_2(\text{NCO})_2$  and  $\text{Ti}(\text{dik})_2(\text{NCS})_2$  complexes are readily hydrolyzed, especially in solution, all syntheses and subsequent handling of the compounds were conducted under anhydrous conditions in a dry nitrogen or argon atmosphere.

**Diisocyanatobis(2,4-pentanedionato)titanium(IV).** A mixture of  $\text{Ti}(\text{acac})_2\text{Cl}_2$ <sup>1</sup> (4.0 g, 12.6 mmol) and dry silver cyanate (6.2 g, 41 mmol) was allowed to reflux for 48 hr in 75 ml of dichloromethane. The resulting brown solution was filtered, and 200 ml of hexane was

added. Cooling overnight in a freezer afforded a gold solid which was collected and dried *in vacuo*; yield, 3.6 g (87% theoretical). Recrystallization from dichloromethane-hexane under an argon atmosphere gave gold needles, mp 124–127° dec. *Anal.* Calcd for  $\text{Ti}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NCO})_2$ : C, 43.66; H, 4.27; N, 8.48; Ti, 14.51. Found: C, 43.64; H, 4.48; N, 8.18; Ti, 14.55. Attempts to prepare this compound in benzene yielded impure products. Solutions of  $\text{Ti}(\text{acac})_2(\text{NCO})_2$  are extremely sensitive to atmospheric moisture.

**Diisothiocyanatobis(2,4-pentanedionato)titanium(IV).** A mixture of  $\text{Ti}(\text{acac})_2\text{Cl}_2$  (4.5 g, 14.2 mmol) and dry sodium thiocyanate (3.6 g, 44 mmol) was allowed to reflux for 12 hr in 250 ml of benzene. The dark red solution was filtered hot and then allowed to stand overnight at  $\sim 5^\circ$ . Filtration of the cold solution gave large, red plates containing benzene of crystallization. The benzene was removed by drying overnight *in vacuo*; yield of  $\text{Ti}(\text{acac})_2(\text{NCS})_2$  3.6 g (70% theoretical). On heating, this compound begins to decompose at 143° and melts at 145–146°. *Anal.* Calcd for  $\text{Ti}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NCS})_2$ : C, 39.78; H, 3.89; N, 7.73; S, 17.70; Ti, 13.22. Found: C, 40.15; H, 4.06; N, 7.66; S, 17.68; Ti, 13.41. This complex is extremely sensitive to moisture and attempts to recrystallize it from benzene or dichloromethane-hexane, even under argon, resulted in extensive hydrolysis. Attempts to prepare this compound in dichloromethane (reflux time 24 hr) gave a red solid which was contaminated with a yellow hydrolysis product.

**Dichlorobis(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(IV).** Titanium(IV) chloride (4.6 ml, 42 mmol) was added slowly with a hypodermic syringe to a solution of dipivaloylmethane (21.9 ml, 107 mmol) in 125 ml of dichloromethane. The red solution was purged with dry nitrogen for 30 min to remove evolved hydrogen chloride. The solution was then boiled down to  $\sim 20$  ml, 250 ml of hexane was added, and the mixture was placed in a freezer overnight. The resulting orange solid (17.0 g, 83% theoretical yield) was filtered and dried *in vacuo*. Recrystallization from dichloromethane-hexane gave orange plates, mp 147–149° dec. *Anal.* Calcd for  $\text{Ti}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2\text{Cl}_2$ : C, 54.44; H, 7.89. Found: C, 54.26; H, 7.96.

**Diisocyanatobis(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(IV).** A mixture of  $\text{Ti}(\text{dpm})_2\text{Cl}_2$  (3.6 g, 7.4 mmol) and dry silver cyanate (4.0 g, 27 mmol) was allowed to reflux for 1 hr in 100 ml of benzene. The resulting light orange solution was filtered and boiled down to  $\sim 20$  ml, and 250 ml of hexane was added. Cooling overnight in a freezer afforded a yellow solid which was filtered and dried *in vacuo*; yield 2.7 g (73%). Recrystallization from benzene-hexane or dichloromethane-hexane gave yellow needles, mp 137–139° dec. *Anal.* Calcd for  $\text{Ti}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2(\text{NCO})_2$ : C, 57.83; H, 7.68; N, 5.62; Ti, 9.61. Found: C, 58.10; H, 8.01; N, 5.21; Ti, 10.05. This compound was also prepared in dichloromethane (reflux time 2 hr).

**Diisothiocyanatobis(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(IV).** A mixture of  $\text{Ti}(\text{dpm})_2\text{Cl}_2$  (3.6 g, 7.4 mmol) and dry sodium thiocyanate (5.0 g, 62 mmol) was allowed to reflux for 6 hr in 200 ml of benzene. The resulting dark red solution was filtered, and the product was isolated in 76% yield (3.0 g) using the same procedure as that employed for  $\text{Ti}(\text{dpm})_2(\text{NCO})_2$ . Recrystallization from benzene-hexane or dichloromethane-hexane gave red-orange plates, mp 127–129° (dec pt 141°). *Anal.* Calcd for  $\text{Ti}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2(\text{NCS})_2$ : C, 54.33; H, 7.22; N, 5.28; S, 12.09; Ti, 9.03. Found: C, 54.34; H, 7.25; N, 5.30; S, 11.94; Ti, 9.25. This compound was also prepared in dichloromethane (reflux time 19 hr).

**Molecular Weight and Conductance Measurements.** Molecular weights were determined cryoscopically in benzene solution using the thermistor apparatus described by Knight, *et al.*<sup>7</sup> Conductance measurements were made in nitrobenzene at  $25.00 \pm 0.05^\circ$  with an Industrial Instruments Model RC 16B2 conductivity bridge and a Freas-type solution cell with bright platinum electrodes. The bridge frequency was 60 Hz, and the cell constant,  $0.1076 \text{ cm}^{-1}$ .

**Infrared Spectra.** Infrared spectra were recorded in the region 4000–300  $\text{cm}^{-1}$  with a Perkin-Elmer 521 grating spectrophotometer. The complexes were studied as Nujol mulls supported between cesium iodide plates and as dichloromethane solutions (10 g/100 ml) in 0.1-mm cesium bromide cells. The estimated uncertainty in reported frequencies is  $\pm 4 \text{ cm}^{-1}$  above 800  $\text{cm}^{-1}$  and about  $\pm 2 \text{ cm}^{-1}$  below 800  $\text{cm}^{-1}$ , where spectra were run on a fivefold expanded frequency scale.

For measurement of the integrated intensity of CN stretching bands, the spectrophotometer was operated in the linear absorbance mode on an expanded frequency scale (10  $\text{cm}^{-1}/\text{cm}$  of chart length). Integrated intensities were calculated by Ramsay's method of direct integration.<sup>8</sup>

Table I. Proton Chemical Shift Data<sup>a</sup>

Compd	Dichloromethane		Deuteriochloroform	
	–CH=	–CH <sub>3</sub>	–CH=	–CH <sub>3</sub>
$\text{Ti}(\text{acac})_2(\text{NCO})_2$	–5.97	–2.11	–5.92	–2.14
$\text{Ti}(\text{acac})_2(\text{NCS})_2$	–6.02	–2.17	–5.97	–2.18
$\text{Ti}(\text{dpm})_2\text{Cl}_2$	–6.20	–1.19	–6.17	–1.19
$\text{Ti}(\text{dpm})_2(\text{NCO})_2$	–6.23	–1.21	–6.18	–1.21
$\text{Ti}(\text{dpm})_2(\text{NCS})_2$	–6.16	–1.17	–6.13	–1.18

<sup>a</sup> In ppm ( $\pm 0.01$ ) relative to an internal reference of tetramethylsilane (1% by volume) at 39°. Concentration of compounds is  $\sim 20$  g/100 ml of solvent.

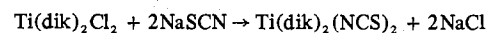
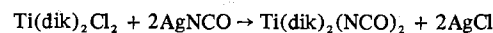
**Nuclear Magnetic Resonance Spectra.** Proton magnetic resonance (pmr) spectra were obtained with a Varian A-60A spectrometer. For determination of chemical shifts, the magnetic field sweep was calibrated with a standard sample of chloroform and tetramethylsilane in carbon tetrachloride, and spectra were recorded in triplicate. Chemical shifts reported in Table I are average values.

Variable-temperature spectra of degassed dichloromethane solutions were recorded in the temperature range +40 to  $-110^\circ$  at a sweep width of 50 Hz. Probe temperatures were determined from the chemical shift between the nonequivalent protons of methanol.<sup>9</sup> Rate constants  $k$  for exchange of acetylacetonate methyl groups (or dpm *tert*-butyl groups) between the two nonequivalent environments of the *cis*- $\text{Ti}(\text{dik})_2\text{X}_2$  complexes were determined by quantitative comparison of experimental spectra with theoretical spectra calculated using the Gutowsky-Holm total line shape equation.<sup>10</sup> Spectra were compared with respect to the following characteristic line shape parameters which were used to determine an average value of  $k$  at each temperature: line widths at one-fourth ( $\Delta_{1/4}$ ), half ( $\Delta_{1/2}$ ), and three-fourths ( $\Delta_{3/4}$ ) maximum amplitude; and, below coalescence,  $\delta\nu_e$ , the frequency separation between the two absorption maxima, and  $r$ , the ratio of the maximum amplitude to the central minimum. Because the transverse relaxation times  $T_2$  were temperature dependent, theoretical line shapes were computed for a range of  $T_2$ 's, and the experimental line shape at each temperature was compared with a theoretical line shape computed using a value of  $T_2$  appropriate to that temperature.  $T_2$  values were obtained by extrapolating plots of  $\log \Delta_{1/2}$  vs.  $1/T$  from the fast- and slow-exchange regions into the coalescence region. The observed frequency separation  $\delta\nu$  between the two resonances in the slow-exchange region was essentially independent of temperature. The procedures used to eliminate or minimize the common sources of error in nmr line broadening studies<sup>11</sup> are detailed in a previous paper.<sup>12</sup>

**Dipole Moment Measurements.** Using a method described previously,<sup>3</sup> dipole moments were determined for  $\text{Ti}(\text{dpm})_2(\text{NCO})_2$  and  $\text{Ti}(\text{dpm})_2(\text{NCS})_2$  in dilute benzene solution at  $25.0 \pm 0.1^\circ$ . The slopes,  $\alpha$ ,  $\beta$ , and  $\gamma$ , respectively, of linear plots of the dielectric constant,  $\epsilon_{12}$ , specific volume,  $v_{12}$ , and refractive index,  $n_{12}$ , of the solution vs. weight fraction of the solute,  $w_2$ , were evaluated by least-squares analysis. Total molar polarizations,  $\tau P_2$ , were obtained from the Halverstadt-Kumler equation,<sup>13</sup> and electronic molar polarizations,  $\epsilon P_2$ , from the modified Halverstadt-Kumler equation.<sup>14</sup> An estimated value of 30  $\text{cm}^3$  was used for the atomic polarization,  $\Delta P_2$ .<sup>15</sup> Dipole moments were calculated from the relation  $\mu = 3/2 [kT_0 P_2 / \pi N]^{1/2}$  where the orientation molar polarization is given by  $OP_2 = \tau P_2 - \epsilon P_2 - \Delta P_2$ , and the symbols  $k$ ,  $T$ , and  $N$  have their usual significance. Results are presented in Table II.

## Results and Discussion

**Synthesis, Characterization, and Stereochemistry.** Dipseudohalobis( $\beta$ -diketonato)titanium(IV) complexes of the type  $\text{Ti}(\text{dik})_2(\text{NCO})_2$  and  $\text{Ti}(\text{dik})_2(\text{NCS})_2$  (dik = acac or dpm) have been prepared in high yields by reaction of the dichloro analogs with an excess of silver cyanate or sodium thiocyanate in refluxing benzene or dichloromethane.



$\text{Ti}(\text{acac})_2\text{Cl}_2$  was described earlier;<sup>1</sup>  $\text{Ti}(\text{dpm})_2\text{Cl}_2$  has been synthesized and characterized in this work. Attempts to prepare related compounds of the type  $\text{Ti}(\text{acac})_2\text{X}_2$  (X = CN, N<sub>3</sub>, SeCN, or NO<sub>2</sub>) by reaction of NaCN, NaN<sub>3</sub>, KSeCN,

Table II. Dipole Moment Data

$10^3 w_2$	$\epsilon_{12}$	$\nu_{12}$	$n_{12}$
Ti(dpm) <sub>2</sub> (NCO) <sub>2</sub> <sup>a,c</sup>			
1.852	2.2951	1.1458	1.49797
2.655	2.3028	1.1444	1.49800
3.667	2.3130	1.1452	1.49812
4.951	2.3285	1.1445	1.49815
6.419	2.3462	1.1427	1.49823
7.434	2.3625		1.49826
8.956	2.3767	1.1415	1.49839
Ti(dpm) <sub>2</sub> (NCS) <sub>2</sub> <sup>b,c</sup>			
1.623	2.2987	1.1445	1.49804
2.887	2.3144	1.1444	1.49824
4.444	2.3379		1.49838
5.620	2.3520	1.1437	1.49843
7.106	2.3753	1.1429	1.49874
8.372	2.3937	1.1423	1.49877
10.599	2.4309	1.1401	1.49903

<sup>a</sup>  $\alpha = 11.84 \pm 0.81$ ;  $\beta = -0.58 \pm 0.29$ ;  $\gamma = 0.06 \pm 0.01$ ;  $T_P = 1193 \pm 87 \text{ cm}^3$ ;  $P_2 = 100 \pm 43 \text{ cm}^3$ ;  $O_P = 1064 \pm 76 \text{ cm}^3$ ;  $\mu = 7.22 \pm 0.26 \text{ D}$ . <sup>b</sup>  $\alpha = 14.66 \pm 0.79$ ;  $\beta = -0.46 \pm 0.22$ ;  $\gamma = 0.11 \pm 0.02$ ;  $T_P = 1571 \pm 86 \text{ cm}^3$ ;  $P_2 = 139 \pm 35 \text{ cm}^3$ ;  $O_P = 1402 \pm 79 \text{ cm}^3$ ;  $\mu = 8.28 \pm 0.23 \text{ D}$ . <sup>c</sup> Errors are estimated at the 95% confidence level.

Table III. Molecular Weight and Conductance Data

Compd	Mol wt data		Conductance data		
	Molar-ity $\times 10^2$	Found <sup>a</sup>	Calcd	Molar-ity $\times 10^3$	$\Delta^b$
Ti(acac) <sub>2</sub> (NCO) <sub>2</sub>	7.18	302	330	4.24	0.17
Ti(acac) <sub>2</sub> (NCS) <sub>2</sub>		c	362	4.20	0.75
Ti(dpm) <sub>2</sub> Cl <sub>2</sub>	4.19	515	485	4.37	0.075
Ti(dpm) <sub>2</sub> (NCO) <sub>2</sub>	2.93	511	498	3.45	0.16
Ti(dpm) <sub>2</sub> (NCS) <sub>2</sub>	4.08	510	531	2.49	0.43

<sup>a</sup> Determined cryoscopically in benzene. <sup>b</sup> Molar conductance,  $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , in nitrobenzene at  $25.00 \pm 0.05^\circ$ . <sup>c</sup> Too insoluble for measurement.

or KNO<sub>2</sub> with Ti(acac)<sub>2</sub>Cl<sub>2</sub> in refluxing benzene or dichloromethane were unsuccessful; only starting materials were isolated after reaction times of 24–48 hr.

Except for Ti(acac)<sub>2</sub>(NCS)<sub>2</sub>, which is only slightly soluble in benzene, the new complexes are very soluble in benzene, dichloromethane, and chloroform; they are nearly insoluble in saturated hydrocarbons. Solutions are extremely sensitive to atmospheric moisture. The following order of decreasing ease of hydrolysis was established by exposing dichloromethane solutions (20 g/100 ml) to the atmosphere until turbidity appeared (times in parentheses): Ti(acac)<sub>2</sub>(NCS)<sub>2</sub> (<2 sec) > Ti(acac)<sub>2</sub>(NCO)<sub>2</sub> (~20 sec) > Ti(dpm)<sub>2</sub>(NCO)<sub>2</sub> (~1 hr) > Ti(dpm)<sub>2</sub>Cl<sub>2</sub> (~2 hr) > Ti(dpm)<sub>2</sub>(NCS)<sub>2</sub> (~4.5 hr). The solid complexes are more stable in air, but hydrolysis is complete after several days' exposure.

Molecular weight and conductance data (Table III) indicate that these complexes are monomeric nonelectrolytes in solution. The small amount of dissociation that does occur in nitrobenzene (<3%) probably involves NCX<sup>-</sup> (or Cl<sup>-</sup>) ion dissociation predominantly since molar conductances for the corresponding alkoxide complexes, Ti(dik)<sub>2</sub>(OR)<sub>2</sub>, are <0.01  $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Infrared spectra of the Ti(dik)<sub>2</sub>(NCX)<sub>2</sub> complexes in the chelating carbonyl stretching region (1300–1600  $\text{cm}^{-1}$ ) are similar to spectra of other metal  $\beta$ -diketonate complexes,<sup>16</sup> and no bands are observed in the 1600–1750- $\text{cm}^{-1}$  region. Therefore, all carbonyl groups are coordinated which, taken together with the molecular weight and conductance results, implies that these compounds are neutral, six-coordinate complexes of the type [Ti(dik)<sub>2</sub>(NCX)<sub>2</sub>].

The following evidence indicates that the Ti(dik)<sub>2</sub>(NCX)<sub>2</sub> complexes have a cis octahedral configuration in solution: (1)

Table IV. Rate Constants for Exchange of Acetylacetonate Methyl Groups or Dipivaloylmethanate *tert*-Butyl Groups in Ti(dik)<sub>2</sub>X<sub>2</sub> Complexes<sup>a</sup>

Ti(acac) <sub>2</sub> (NCO) <sub>2</sub> <sup>b</sup>		Ti(dpm) <sub>2</sub> (NCO) <sub>2</sub> <sup>c</sup>		Ti(dpm) <sub>2</sub> Cl <sub>2</sub> <sup>d</sup>	
Temp, °C	$k$ , sec <sup>-1</sup>	Temp, °C	$k$ , sec <sup>-1</sup>	Temp, °C	$k$ , sec <sup>-1</sup>
-25.7	24.6	-32.2	133	-17.6	151
-35.2	9.2	-39.7	62	-23.2	82
-38.0	7.3	-44.8	45	-26.5	61
-40.6	5.6	-47.6	34	-30.3	46
-43.7	4.5	-49.9	26	-32.8	33
-44.1	4.2	-51.4	21.6	-37.4	22.6
-44.5	3.9	-53.9	16.7	-37.8	22.2
-45.0	3.8	-56.4	13.9	-40.2	16.9
-46.8	3.2	-58.2	11.3	-43.0	11.0
-49.0	2.3	-60.5	8.5	-45.4	9.5
-53.2	1.4	-67.3	3.8	-49.4	5.6
				-55.1	3.1

<sup>a</sup> In dichloromethane solution. <sup>b</sup> Concentration 0.560 *M*. The frequency separation in the slow-exchange limit,  $\delta\nu$ , is 3.05 Hz. The coalescence temperature,  $T_c$ , is  $-43^\circ$ . <sup>c</sup> Concentration 0.416 *M*;  $\delta\nu = 10.53 \text{ Hz}$ ;  $T_c = -51^\circ$ . <sup>d</sup> Concentration 0.398 *M*;  $\delta\nu = 12.50 \text{ Hz}$ ;  $T_c = -34^\circ$ .

Table V. Concentration Dependence of Rate Constants for Exchange of Methyl or *tert*-Butyl Groups<sup>a</sup>

Compd	Concn, <i>M</i>	$k$ , sec <sup>-1</sup>	
		-28.0°	-40.4°
Ti(acac) <sub>2</sub> (NCO) <sub>2</sub>	0.33	16	5.9
	0.12	19	5.6
Ti(dpm) <sub>2</sub> (NCO) <sub>2</sub>	0.17	184	58
	0.08	179	63
Ti(dpm) <sub>2</sub> Cl <sub>2</sub>	0.33	52	17
	0.12	55	17

<sup>a</sup> In dichloromethane solution.

two methyl (or two *tert*-butyl) resonances of equal intensity in low-temperature pmr spectra of dichloromethane solutions (see Figure 1), (2) two CN stretching frequencies, separated by  $\sim 40\text{--}50 \text{ cm}^{-1}$ , in infrared spectra of dichloromethane solutions (Table VII), and (3) dipole moments in benzene solution of  $7.22 \pm 0.26 \text{ D}$  for Ti(dpm)<sub>2</sub>(NCO)<sub>2</sub> and  $8.28 \pm 0.23 \text{ D}$  for Ti(dpm)<sub>2</sub>(NCS)<sub>2</sub> (Table II). The probable configuration in the solid state is also cis since infrared spectra of Nujol mulls exhibit two CN stretching bands and are, in general, closely similar to the solution spectra (Tables VII and VIII). Infrared bands of the pseudohalide ligands will be discussed in the section on vibrational spectra; suffice it to say at this point that the NCX frequencies and integrated absorption intensities point to an N-bonded attachment of the pseudohalide ligands.

Like the corresponding acetylacetonate complex,<sup>1,3</sup> Ti(dpm)<sub>2</sub>Cl<sub>2</sub> also has a cis structure in solution. Two *tert*-butyl resonances of equal intensity are observed in low-temperature pmr spectra, and the molecule has a dipole moment (in CCl<sub>4</sub> solution) of  $8.08 \pm 0.45 \text{ D}$ .<sup>17</sup>

**Configurational Rearrangements.** Pmr spectra of Ti(dpm)<sub>2</sub>Cl<sub>2</sub> and the Ti(dik)<sub>2</sub>(NCX)<sub>2</sub> complexes exhibit line broadening owing to rapid exchange of acetylacetonate methyl groups (or dpm *tert*-butyl groups) between the two non-equivalent environments of the cis isomer. Two methyl (or two *tert*-butyl) resonances are observed at low temperatures, but only a single, time-averaged resonance is seen at high temperatures. Representative spectra are presented in Figure 1, and first-order rate constants  $k$  for the exchange process for Ti(acac)<sub>2</sub>(NCO)<sub>2</sub>, Ti(dpm)<sub>2</sub>(NCO)<sub>2</sub>, and Ti(dpm)<sub>2</sub>Cl<sub>2</sub> are listed in Table IV. The rate constants are independent of concentration (see Table V), as expected for first-order kinetics. Precise rate constants for the Ti(dik)<sub>2</sub>(NCS)<sub>2</sub> complexes could not be determined because the coalescence temperatures are near the freezing point of the solvent and limiting spectra in

Table VI. Kinetic Data for Methyl or *tert*-Butyl Group Exchange in  $\text{Ti}(\text{dik})_2\text{X}_2$  Complexes<sup>a</sup>

Compd	$k_{25^\circ}$ , $\text{sec}^{-1}$	$k_{-43^\circ}$ , $\text{sec}^{-1}$	$\Delta G^*(-43^\circ)$ , kcal/mol	$\Delta H^*$ , kcal/mol	$\Delta S^*$ , eu	$E_a$ , kcal/mol	log A
$\text{Ti}(\text{acac})_2(\text{NCO})_2$	$1.1 \times 10^3$	4.5	$12.67 \pm 0.05^b$	$10.5 \pm 0.6$	$-9.3 \pm 2.4$	$11.0 \pm 0.6$	$11.08 \pm 0.52$
$\text{Ti}(\text{acac})_2\text{F}_2^c$	$1.6 \times 10^4$	$4.9 \times 10$	$11.58 \pm 0.04$	$11.1 \pm 0.4$	$-2.2 \pm 2.0$	$11.6 \pm 0.5$	$12.70 \pm 0.49$
$\text{Ti}(\text{acac})_2\text{Cl}_2^c$	$6.7 \times 10^2$	2.5	$12.93 \pm 0.06$	$10.7 \pm 0.6$	$-9.7 \pm 2.3$	$11.2 \pm 0.6$	$11.03 \pm 0.51$
$\text{Ti}(\text{acac})_2\text{Br}_2^c$	$2.3 \times 10^3$	7.2	$12.45 \pm 0.04$	$11.0 \pm 0.5$	$-6.2 \pm 2.0$	$11.6 \pm 0.4$	$11.85 \pm 0.36$
$\text{Ti}(\text{acac})_2\text{I}_2$		$3 \times 10^2^d$					
$\text{Ti}(\text{dpm})_2(\text{NCS})_2$		$6 \times 10^3^e$					
$\text{Ti}(\text{dpm})_2(\text{NCO})_2$	$6.7 \times 10^3$	$5.0 \times 10^1$	$11.57 \pm 0.04$	$9.4 \pm 0.3$	$-9.5 \pm 1.5$	$9.8 \pm 0.3$	$11.04 \pm 0.32$
$\text{Ti}(\text{dpm})_2\text{Cl}_2$	$3.5 \times 10^3$	$1.2 \times 10^1$	$12.22 \pm 0.05$	$10.9 \pm 0.4$	$-5.6 \pm 1.5$	$11.4 \pm 0.4$	$11.91 \pm 0.33$

<sup>a</sup> In dichloromethane solution. <sup>b</sup> All errors are random errors estimated at the 95% confidence level. <sup>c</sup> Arrhenius parameters are taken from ref 1; Eyring parameters were obtained from  $\log(k/T)$  vs.  $1/T$  plots. <sup>d</sup> Extrapolated value based on  $k_{-64^\circ} = 25 \text{ sec}^{-1}$  and an assumed activation energy of 11 kcal/mol. <sup>e</sup> Extrapolated value based on  $k_{-100^\circ} = 23 \text{ sec}^{-1}$  and an assumed log A of 11.04, the value for  $\text{Ti}(\text{dpm})_2(\text{NCO})_2$ .

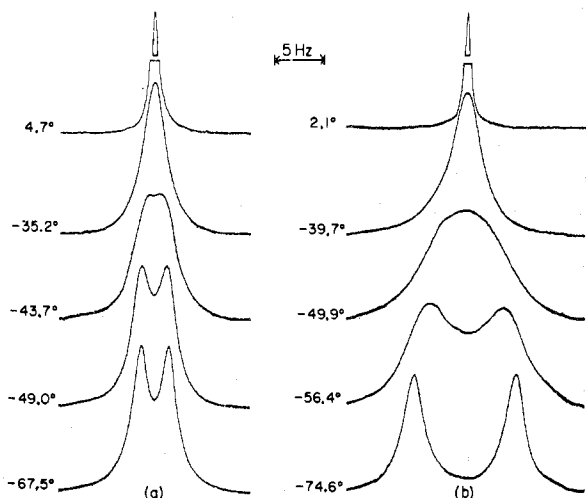


Figure 1. (a) Methyl region of pmr spectra for  $\text{Ti}(\text{acac})_2(\text{NCO})_2$  in dichloromethane. (b) *tert*-Butyl region of pmr spectra for  $\text{Ti}(\text{dpm})_2(\text{NCO})_2$  in dichloromethane.

the slow-exchange region could not be observed. An approximate rate constant of  $23 \text{ sec}^{-1}$  for  $\text{Ti}(\text{dpm})_2(\text{NCS})_2$  at the coalescence temperature of  $\sim -100^\circ$  was estimated on the assumption that  $\text{Ti}(\text{dpm})_2(\text{NCS})_2$  and  $\text{Ti}(\text{dpm})_2(\text{NCO})_2$  have the same frequency separation (10.53 Hz) in the slow-exchange limit. Arrhenius and Eyring activation parameters were obtained in the usual way from the least-squares straight lines of  $\log k$  vs.  $1/T$  plots (Figure 2) and  $\log(k/T)$  vs.  $1/T$  plots, respectively. The activation parameters are presented in Table VI along with extrapolated values of  $k$  at  $25^\circ$  and values of  $k$  and  $\Delta G^*$  at a common temperature in the coalescence region ( $-43^\circ$ ). Also included in Table VI, for comparison, are kinetic data for  $\text{Ti}(\text{acac})_2\text{X}_2$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ).<sup>1,4</sup> The rate constants increase by  $\sim 10^3$  as the halogen or pseudohalogen varies in the order  $\text{Cl} < \text{NCO} < \text{Br} < \text{F} < \text{I} < \text{NCS}$ . For complexes which contain the same monodentate ligand, viz.,  $\text{Ti}(\text{dik})_2(\text{NCO})_2$  and  $\text{Ti}(\text{dik})_2\text{Cl}_2$  ( $\text{dik} = \text{acac}$  or  $\text{dpm}$ ), the  $\text{dpm}$  complexes rearrange  $\sim 5$ – $10$  times faster than the  $\text{acac}$  analogs.

Possible mechanisms for rearrangement of these complexes include (1) complete dissociation of one diketonate ligand to give a four-coordinate intermediate, (2) dissociation of a halide or pseudohalide ion to give a five-coordinate intermediate, (3) rupture of one Ti–O bond to give a five-coordinate intermediate containing one monodentate diketonate ligand, and (4) twisting mechanisms which effect rearrangement without metal–ligand bond rupture. Rearrangement of the pseudohalide complexes via the intermolecular mechanisms, mechanisms 1 and 2, is ruled out by the following experimental results. (1) PMR spectra of  $\text{CDCl}_3$  solutions which are  $\sim 0.2 \text{ M}$  in  $\text{Ti}(\text{dpm})_2(\text{NCX})_2$  ( $\text{NCX} = \text{NCO}$  or  $\text{NCS}$ ) and  $\sim 0.6 \text{ M}$  in free dipivaloylmethane show an unbroadened  $-\text{CH}=\text{}$  resonance for the complex and a separate, unbroadened  $-\text{CH}=\text{}$  resonance for the enol form of  $\text{H}(\text{dpm})$  at ambient probe temperature

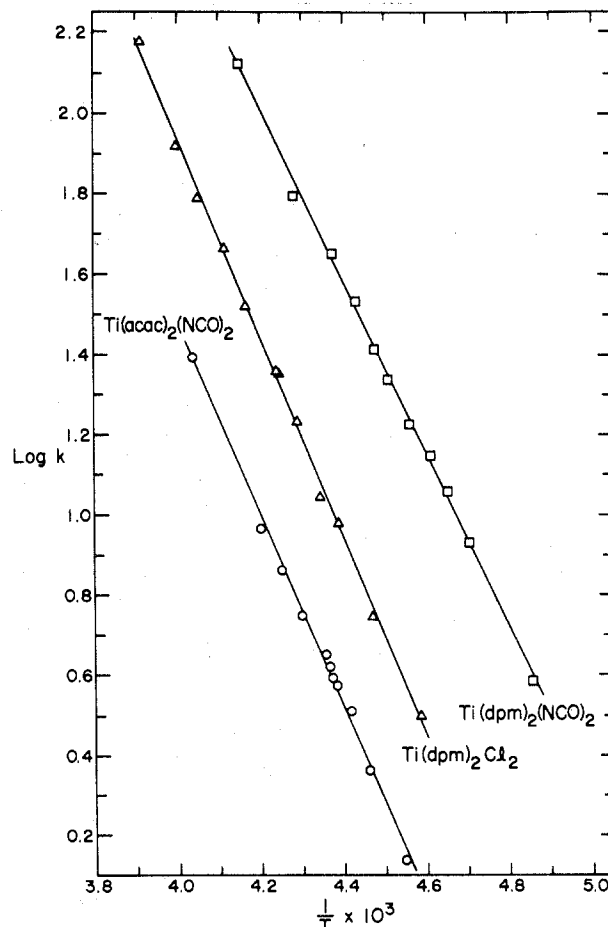


Figure 2. Arrhenius plots for exchange of nonequivalent methyl (or *tert*-butyl) groups in  $\text{Ti}(\text{dik})_2\text{X}_2$  complexes.

of  $\sim 39^\circ$ . Thus, complete dissociation of diketonate ligands is slow on the nmr time scale at a temperature  $90$ – $140^\circ$  above the coalescence temperatures for exchange of *tert*-butyl groups in the complexes. (2) The  $-\text{CH}=\text{}$  region of pmr spectra of an equimolar mixture of  $\text{Ti}(\text{dpm})_2(\text{NCO})_2$  and  $\text{Ti}(\text{dpm})_2(\text{NCS})_2$  in  $\text{CDCl}_3$  (initial concentrations  $\sim 0.4 \text{ M}$ ) indicates that random scrambling of NCX ligands does occur to give a statistical equilibrium mixture of reactants and the mixed-ligand complex  $\text{Ti}(\text{dpm})_2(\text{NCO})(\text{NCS})$ . However, about 15 min is required to reach equilibrium at  $\sim 39^\circ$  and therefore the rate of pseudohalide dissociation is slow compared with the rate of *tert*-butyl group exchange. Similar experiments have been described previously<sup>1</sup> which rule out mechanisms 1 and 2 for the corresponding dihalo complexes,  $\text{Ti}(\text{acac})_2\text{X}_2$ .

The trends in the rearrangement rates (Table VI) are somewhat surprising, and these trends provide no reliable basis on which to choose between a one-bond rupture mechanism and a twist mechanism. First, the faster rates for the  $\text{dpm}$

Table VII. NCX and Ti-NCX Vibrational Frequencies ( $\text{cm}^{-1}$ ) for  $\text{Ti}(\text{dik})_2(\text{NCX})_2$  Complexes

$\text{Ti}(\text{acac})_2(\text{NCO})_2$		$\text{Ti}(\text{acac})_2(\text{NCS})_2$	$\text{Ti}(\text{dpm})_2(\text{NCO})_2$		$\text{Ti}(\text{dpm})_2(\text{NCS})_2$		Assignment
Nujol	Soln <sup>a</sup>	Nujol <sup>b</sup>	Nujol	Soln <sup>a</sup>	Nujol	Soln <sup>a</sup>	
2220 vs <sup>c,d</sup>	2220 (8) <sup>f</sup>	2040 vs	2215 vs <sup>e</sup>	2214 (8) <sup>f</sup>	2030 vs	2032 (10) <sup>f</sup>	$\nu(\text{CN})$
2170 vs <sup>d</sup>	2175 (11) <sup>f</sup>	1997 vs	2170 vs <sup>e</sup>	2173 (11) <sup>f</sup>	1980 vs	1980 (15) <sup>f</sup>	$\nu(\text{CN})$
g	1383 m	911 w	g	1379 m	904 w	903 vw	$\nu(\text{CX})$
		883 w			895 w	890 vw	
1227 w	1230 w		h	h			$2\delta(\text{NCX})$
625 m, sp	620 m	493 m, sp	619 m, sp	h	498 vw, sp	h	$\delta(\text{NCX})$
616 m, sp		486 m, sp			484 vw, sp	h	
413 s	428 s, b	377 s	432 s, b	435 s, b	391 sh	393 sh	$\nu(\text{Ti-NCX})$
399 s	405 m	361 s			380 s	380 s	$\nu(\text{Ti-NCX})$

<sup>a</sup> In dichloromethane (10 g/100 ml). <sup>b</sup> Only solid-state spectra could be obtained for  $\text{Ti}(\text{acac})_2(\text{NCS})_2$  owing to rapid hydrolysis in solution. <sup>c</sup> Key: s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad; sp, sharp. <sup>d</sup>  $\nu(\text{CN}) + \nu(\text{CX})$  combination bands were observed at 3600 and 3555  $\text{cm}^{-1}$ . <sup>e</sup>  $\nu(\text{CN}) + \nu(\text{CX})$  combination bands were observed at 3590 and 3550  $\text{cm}^{-1}$ . <sup>f</sup> Integrated absorption intensity  $\times 10^{-4} M^{-1} \text{cm}^{-2}$ , per mole of NCX for each band of the doublet. <sup>g</sup> Obscured by Nujol absorption. <sup>h</sup> Obscured by nearby, more intense band.

complexes, relative to the acac analogs, are surprising since the electron-releasing *tert*-butyl groups should produce a relative strengthening of the Ti-O bonds in the dpm compounds. Even more surprising is the fact that the rate of trifluoromethyl group exchange in the hexafluoroacetylacetonate complex *cis*- $\text{Ti}(\text{hfac})_2\text{Cl}_2$ <sup>18</sup> is only slightly faster than the rearrangement rates in the dpm and acac analogs; at the coalescence temperature of  $-10^\circ$ ,  $k = 290 \text{ sec}^{-1}$  for  $\text{Ti}(\text{hfac})_2\text{Cl}_2$  compared with 275  $\text{sec}^{-1}$  for  $\text{Ti}(\text{dpm})_2\text{Cl}_2$  and 55  $\text{sec}^{-1}$  for  $\text{Ti}(\text{acac})_2\text{Cl}_2$ . These results contrast with the behavior of aluminum(III) and gallium(III) tris( $\beta$ -diketonates) where introduction of a hfac ligand results in a large (factor of  $\sim 10^4$ ) increase in rearrangement rate.<sup>19</sup> Our results are difficult to rationalize, especially on the basis of a bond-rupture mechanism. On the other hand, the halogen (pseudohalogen) dependence of the rates ( $\text{Cl} < \text{NCO} < \text{Br} < \text{F} < \text{I} < \text{NCS}$ ) is not easily rationalized in terms of a twist mechanism since the observed, irregular order does not correlate well with the size or electronic properties of the monodentate ligand. Finally, the relatively large difference (factor of  $\sim 10^2$ ) between the rearrangement rates for the NCO and NCS complexes is a bit enigmatic in view of the fact that both pseudohalide ligands are N bonded.<sup>20</sup>

**Vibrational Spectra.** Infrared frequencies for the  $\text{Ti}(\text{dik})_2(\text{NCX})_2$  complexes in the solid state and in dichloromethane solution are listed in Tables VII and VIII.<sup>21</sup> Also included in Table VIII, for comparison, are frequencies for the corresponding dichloro complexes. Assignments for  $\beta$ -diketonate and metal-oxygen vibrations are based on normal-coordinate treatments of metal acetylacetonates<sup>22,23</sup> and studies of the frequency shifts which occur upon isotopic substitution.<sup>22-26</sup> Assignments for the acac ligand vibrations follow closely those given earlier for the dihalobis(acetylacetonato) complexes of Zr(IV),<sup>27</sup> Hf(IV),<sup>27</sup> and Sn(IV).<sup>12</sup> dpm ligand vibrations were assigned by comparing spectra of the dpm complexes with spectra of the acac analogs; in addition to frequencies characteristic of the chelate ring, the dpm complexes exhibit characteristic *tert*-butyl skeletal frequencies.<sup>28</sup> Unique bands in spectra of the  $\text{Ti}(\text{dik})_2(\text{NCX})_2$  complexes (Table VII), which are not present in spectra of the  $\text{Ti}(\text{dik})_2\text{Cl}_2$  analogs, were assigned to NCX vibrations on the basis of previously published work.<sup>29-37</sup>

Burmeister<sup>29</sup> has summarized the NCS frequency shifts to be expected for N-bonded and S-bonded thiocyanate complexes. Relative to the free-ion values ( $\nu(\text{CS})$  749  $\text{cm}^{-1}$ ,  $\delta(\text{NCS})$  486 and 471  $\text{cm}^{-1}$  in  $\text{KSCN}$ ), N bonding produces an increase in the CS stretching frequency (to 780–860  $\text{cm}^{-1}$ ) but only a small change in the SCN bending frequency (to 440–490  $\text{cm}^{-1}$ ), while S bonding gives a decrease in both frequencies (to 690–720 and 400–440  $\text{cm}^{-1}$ , respectively). In addition, the integrated intensity of the CN stretching band increases from the free-ion value of  $4.4 \times 10^4 M^{-1} \text{cm}^{-2}$  to

$\sim 10 \times 10^4 M^{-1} \text{cm}^{-2}$  in N-bonded complexes but decreases to  $\sim 1 \times 10^4 M^{-1} \text{cm}^{-2}$  in S-bonded complexes.<sup>30</sup> The  $\text{Ti}(\text{dik})_2(\text{NCS})_2$  complexes (Table VII) exhibit a  $\nu(\text{CS})$  doublet near 900  $\text{cm}^{-1}$ , a  $\delta(\text{NCS})$  doublet near 490  $\text{cm}^{-1}$ , and integrated intensities for the  $\nu(\text{CN})$  bands of  $(10-15) \times 10^4 M^{-1} \text{cm}^{-2}$ . These features of the spectra are clearly in accord with an N-bonded attachment of the thiocyanate ligands. Further evidence for N bonding is provided by the unusually low CN stretching frequencies (2040 and 1997  $\text{cm}^{-1}$  for  $\text{Ti}(\text{acac})_2(\text{NCS})_2$ ; 2030 and 1980  $\text{cm}^{-1}$  for  $\text{Ti}(\text{dpm})_2(\text{NCS})_2$ ); CN stretching frequencies are generally  $\leq 2100 \text{ cm}^{-1}$  for N-bonded complexes and  $\geq 2100 \text{ cm}^{-1}$  for S-bonded complexes.<sup>29</sup> The low CN frequencies and high CS frequencies are in keeping with the high oxidation state of titanium(IV)<sup>31</sup> and its  $d^0$  electronic configuration. The observed mode of NCS attachment is in accord with the fact that titanium(IV) is a class a acceptor<sup>38</sup> (hard acid<sup>39</sup>).

An N-bonded attachment of the cyanate ligands in the  $\text{Ti}(\text{dik})_2(\text{NCO})_2$  complexes may be assigned on the basis of a CO stretching frequency near 1380  $\text{cm}^{-1}$  (Table VII); for N-bonded NCO,  $\nu(\text{CO})$  is greater than 1300  $\text{cm}^{-1}$ , while for the quite rare O-bonded attachment  $\nu(\text{CO})$  is expected to lie below 1200  $\text{cm}^{-1}$ .<sup>32-37</sup> Observation of combination bands ( $\nu(\text{CO}) + \nu(\text{CN})$ ) near 3600  $\text{cm}^{-1}$  serves to confirm our assignment of the  $\nu(\text{CO})$  fundamental.<sup>32,33</sup> For example,  $\text{Ti}(\text{acac})_2(\text{NCO})_2$  exhibits two combination bands at 3600  $\text{cm}^{-1}$  (1383 + 2220) and 3555  $\text{cm}^{-1}$  (1383 + 2170). The  $\nu(\text{CN})$  and  $\delta(\text{NCO})$  frequencies ( $\delta(\text{NCO}) \sim 620 \text{ cm}^{-1}$ ) are of no help in distinguishing the mode of NCO attachment; however, the integrated intensities of the  $\nu(\text{CN})$  bands,  $(\sim 8-11) \times 10^4 M^{-1} \text{cm}^{-2}$ , are larger than the free-ion value, in accord with previous reports for N-bonded cyanate complexes.<sup>32,34</sup>

As was mentioned earlier, the presence of two CN stretching bands in solid-state and solution spectra of the  $\text{Ti}(\text{dik})_2(\text{NCX})_2$  complexes indicates that these compounds exist as the *cis* isomer in the solid state as well as in solution. Consistent with this stereochemistry, the strong M-NCO stretching bands (400–435  $\text{cm}^{-1}$ ) and the M-NCS stretching bands (360–395  $\text{cm}^{-1}$ ) either are very broad or are split into two components.

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**Registry No.**  $\text{Ti}(\text{acac})_2(\text{NCO})_2$ , 53293-30-4;  $\text{Ti}(\text{acac})_2(\text{NCS})_2$ , 53293-31-5;  $\text{Ti}(\text{dpm})_2\text{Cl}_2$ , 53293-32-6;  $\text{Ti}(\text{dpm})_2(\text{NCO})_2$ , 53293-33-7;  $\text{Ti}(\text{dpm})_2(\text{NCS})_2$ , 53293-34-8;  $\text{Ti}(\text{acac})_2\text{Cl}_2$ , 16986-94-0.

**Supplementary Material Available.** Table VIII, a listing of frequencies and assignments for the  $\beta$ -diketonate and metal-ligand vibrations of  $\text{Ti}(\text{dik})_2\text{X}_2$  (dik = acac or dpm; X = Cl, NCO, or NCS), will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105  $\times$  148 mm, 24 $\times$  reduction,

negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number AIC40539K.

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## Heavy Metal-Nucleotide Reactions. IV. Nature of the Reaction between Mercury(II) and Uridine or Thymidine. Vibrational Spectroscopic Studies on Binding to N(3), C(4)=O, and C(5) of the Uracil Base<sup>1</sup>

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Mercurials can react with uracil, uridine, or thymidine in three different ways: coordination to a carbonyl oxygen of the neutral ligand, electrophilic attack on the ring with displacement of a proton and formation of a mercury-carbon bond, and electrophilic attack with displacement of a proton and formation of a mercury-nitrogen bond. Raman and, in part, infrared spectra have been obtained for model compounds representative of the first two types of binding. The spectra for both of these types of binding are very different from those observed previously for reaction of  $\text{CH}_3\text{Hg}^{\text{II}}$  with Urd in dilute aqueous solution at pH 8, where the spectra suggested the third type of binding reaction occurred. It is concluded that the only important reaction in dilute aqueous solution involves electrophilic attack at N(3) with substitution of the proton by mercury. Changes in the spectra are discussed in terms of LCAO-SCF calculations for the base and the base from which a proton has been lost.

### Introduction

It has been assumed generally that in the pH range 7-9 reaction of mercury(II) or alkylmercury(II) ions with native DNA occurs first at the thymidine base with substitution of the proton on N(3) by  $\text{Hg}^{2+}$  or  $\text{RHg}^+$ .<sup>2-12</sup> The proton which is displaced normally is involved in hydrogen bonding to adenosine in the double helix. Of interest is how mercury(II) is able to interact with such a well-protected site at room temperature. In the case of alkylmercury(II) species, e.g.,  $\text{CH}_3\text{Hg}^+$ , it has been observed that there is a cooperative transition to denatured DNA which occurs above a critical concentration of the alkylmercury(II).<sup>11</sup> The characteristics of this reaction have been summarized recently by Beerman and Lebowitz,<sup>12</sup> who employed  $\text{CH}_3\text{Hg}^{\text{II}}$  to probe for unpaired bases in superhelical DNA.

Mercuric chloride reacts with uracil and dihydrouracil to yield crystalline 1:2 complexes in which the mercury(II) is six-coordinate with four bridging chlorides and two trans

oxygens.<sup>13</sup> Only the C(4)=O oxygens are coordinated to mercury, while the C(2)=O oxygens are involved in intermolecular hydrogen bonding between Ura or  $\text{h}_2\text{Ura}$  molecules. The relatively short Hg-O interaction,  $2.71 \pm 0.02 \text{ \AA}$  for  $\text{HgCl}_2 \cdot 2\text{Ura}$ , together with the distortion of the oxygen out of the least-squares plane of Ura, suggests a rather strong Hg-O bond. If mercury(II) coordinates to the carbonyl oxygen rather than to the ring nitrogen of thymine in DNA, the ready reaction of mercurials with DNA without thermal activation could be explained by attack on the partially exposed C(4)=O oxygen in the large groove of the double helix. This has been discussed by Carrabine and Sundaralingam.<sup>13</sup>

Recently we have observed, using Raman difference spectrophotometry, changes in the spectra of Ura, Urd, and poly(U) upon reaction with  $\text{CH}_3\text{Hg}^{\text{II}}$  which indicated that the proton bound to N(3) was displaced, and mercury appeared to be bound to N(3). These studies were made with solutions at pH 8.<sup>14</sup> Carrabine and Sundaralingam crystallized the