

that the rate expressions for oxygen exchange and for racemization of  $\text{Cr}(\text{ox})_2\text{bipy}^-$  and  $\text{Cr}(\text{ox})_2\text{phen}^-$  are different. When it is remembered that oxygen exchange can proceed entirely by an interchange mechanism and that this does *not* produce racemization, then the dangers in using the two sets of rate data become apparent. Even without an interchange mechanism the general exchange independence of changes in

the central metal (Table IX) indicates that the rate-controlling step is probably attack of water on the carbonyl carbon. This is of no consequence in producing racemization.

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## Synthesis and Characterization of N,N-Dialkyldithiocarbamate Complexes of Niobium(V) and Tantalum(V)

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N,N-Dialkyldithiocarbamate salts react with niobium and tantalum pentahalides in methanol to give compounds with the stoichiometry  $\text{MX}(\text{OCH}_3)_2(\text{S}_2\text{CNR}_2)_2$ . Compounds were prepared in which X was Cl, Br, and NCS and R was  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , and  $\text{CH}_2\text{C}_6\text{H}_5$ . The compounds are air-stable crystalline materials. Solutions of the compounds in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CCl}_4$ , and *t*-butyl alcohol are stable; they decompose in primary alcohols. The compounds are nonelectrolytes and are monomeric. Ultraviolet, infrared, and proton magnetic resonance spectral data are presented.

### Introduction

Few well-characterized crystalline complexes of niobium(V) and tantalum(V) are described in the literature.<sup>1</sup> Of those which are known many are unstable in solution or to the moisture in the atmosphere. The work reported in this paper describes some of our efforts to prepare relatively stable complexes of these elements.

N,N-Dialkyldithiocarbamate salts form complexes with a variety of metal ions. In these complexes the ligand typically coordinates as a bidentate ligand through the two sulfur atoms. Dithiocarbamate complexes of niobium ( $\text{Nb}(\text{S}_2\text{CN}(\text{CH}_3)_2)_3$ ) and tantalum ( $\text{Ta}(\text{S}_2\text{CN}(\text{CH}_3)_2)_3$ ) have been synthesized by the insertion of  $\text{CS}_2$  into Nb–N bonds of dimethylamine complexes of niobium and tantalum.<sup>2</sup> Their properties have not been reported.

### Experimental Section

**Reagents.**—Niobium and tantalum pentahalides were obtained from Alfa Inorganics Inc. Sodium diethyldithiocarbamate was obtained as a certified ACS reagent from Fisher Scientific Co. The dimethylammonium salt of dimethyldithiocarbamic acid and the zinc salt of dibenzoyldithiocarbamic acid were obtained as "highest purity" grade reagents from Eastman Organic Chemicals. All solvents were ACS reagent grade and were dried over molecular sieves.

**Physical Measurements.**—Magnetic susceptibilities were measured at room temperature (25°) by the Gouy method. Conductivities were measured using a fill cell having a cell constant of about  $0.4 \text{ cm}^{-2} \text{ ml}^{-1}$  and an Industrial Instruments Inc. Model RC1B conductivity bridge.

Ultraviolet spectra were recorded on a Cary 14 spectrophotometer. Infrared spectra were recorded in KBr wafers using a Perkin-Elmer Model 257 grating spectrophotometer. Integrated intensities were obtained using Ramsay's method of direct integration.<sup>3</sup> Acetonitrile solutions were used in intensity studies. Nmr spectra were recorded on a Varian T-60 spectrometer using  $\text{CDCl}_3$  and  $\text{CD}_3\text{CN}$  as solvents. For detailed studies a Varian A-60A spectrometer was used.

Molecular weights were determined cryoscopically in sulfolane for the Nb–Cl derivatives. The sulfolane was purified and dried by distillation from powdered KOH under vacuum. Molecular weights were also determined using  $\text{CHCl}_3$  solutions in a Mechrolab Inc. vapor pressure osmometer, Model 301A.

**Methods of Analysis.**—Niobium and tantalum were determined as  $\text{M}_2\text{O}_5$  by igniting the compound in a porcelain crucible. Halide analyses were done by the Volhard method preceded by fusion of the sample with  $\text{Na}_2\text{O}_2$  and NaOH. Carbon, hydrogen, sulfur, and nitrogen analyses were performed by Midwest Micro Lab Inc.

**Preparation of Complexes.**  $\text{NbCl}(\text{OCH}_3)_2(\text{dedtc})_2$ .—A 5.5-g sample of  $\text{NbCl}_5$  (0.02 mol) was weighed out in a 500-ml round-bottom flask in a drybox. Methanol (100 ml) was added. Vigorous evolution of HCl and a clear, colorless solution resulted. A solution of 9.00 g of  $\text{Na}(\text{dedtc}) \cdot 3\text{H}_2\text{O}$  (0.04 mol) in 100 ml of methanol was prepared and added. A clear, dark wine red solution resulted. This solution bleaches over a period of 18–24 hr to a clear, light yellow solution containing large clusters of light yellow crystals. Recrystallization was accomplished by dissolving the compound in  $\text{CCl}_4$ , removing undissolved solid, and reducing the volume with a rotary evaporator until white crystals appeared. The compound was dried under vacuum.

$\text{NbBr}(\text{OCH}_3)_2(\text{dedtc})_2$ .—This compound was prepared in a manner similar to the chloro compound. The product is a white, crystalline compound.

$\text{NbNCS}(\text{OCH}_3)_2(\text{dedtc})_2$ .—A 5.5-g sample of  $\text{NbCl}_5$  (0.02 mol) was dissolved in 100 ml of methanol. To this solution was added 8.1 g of NaSCN (0.10 mol). The solution turned yellow and a

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TABLE I  
 ANALYSES, MOLECULAR WEIGHTS, MELTING POINTS, AND YIELDS

Compound		Analyses, %				mol wt		Mp, °C	Yield, %		
		Nb (Ta)	Halide	S	N	C	H			a	b
NbCl(OCH <sub>3</sub> ) <sub>2</sub> (dmdtc) <sub>2</sub>	Calcd	21.57	8.22	29.76	6.50	22.30	4.23	431		300 (char)	70
	Found	21.39	8.19	29.50		22.14	4.39	423	463		
NbBr(OCH <sub>3</sub> ) <sub>2</sub> (dmdtc) <sub>2</sub>	Calcd	19.55	16.82	26.98	5.89	20.22	3.81	475		300 (char)	70
	Found	19.04	16.32	25.83		19.84	5.88		503		
NbCl(OCH <sub>3</sub> ) <sub>2</sub> (dedtc) <sub>2</sub>	Calcd	19.04	7.28	26.21	5.70	29.52	5.30	486		174	60
	Found	19.10	7.24	26.52	5.81	29.4	5.22	467	503		
NbBr(OCH <sub>3</sub> ) <sub>2</sub> (dedtc) <sub>2</sub>	Calcd	17.42	14.98	24.02	5.31	27.04	4.87	531		180	65
	Found	17.82	14.63	24.33	5.39	27.21	5.02	477	537		
NbNCS(OCH <sub>3</sub> ) <sub>2</sub> (dedtc) <sub>2</sub>	Calcd	18.23		31.46	8.24	30.40	5.14	510		174	75
	Found	18.08		31.40		30.64	5.39		548		
TaCl(OCH <sub>3</sub> ) <sub>2</sub> (dedtc) <sub>2</sub>	Calcd	31.53	6.18	22.30	4.88	25.09	4.56	574		169	10
	Found	31.36	6.41	20.95	4.89	24.88	4.47		486		
TaBr(OCH <sub>3</sub> ) <sub>2</sub> (dedtc) <sub>2</sub>	Calcd	29.29	12.93							173	...
	Found	29.09	12.30								
TaCl(OCH <sub>3</sub> ) <sub>2</sub> (dmdtc) <sub>2</sub>	Calcd	34.81	6.82							280 (char)	20
	Found	31.96	7.55								
NbCl(OCH <sub>3</sub> ) <sub>2</sub> (dbdtc) <sub>2</sub>	Calcd	12.63	4.82	17.44		52.26	4.67	737		159	70
	Found	12.84	4.22	17.67		52.23	4.66	697	753		
NbBr(OCH <sub>3</sub> ) <sub>2</sub> (dbdtc) <sub>2</sub>	Calcd	11.98	10.31	16.50		49.30	4.39	780		162	70
	Found	12.79	11.10	15.94		49.28	4.60		780		

<sup>a</sup> Cryoscopic values. <sup>b</sup> Values by osmometry.

precipitate of NaCl formed. The solution was allowed to stand for 2 hr to ensure complete precipitation of NaCl which was removed by filtration. A solution of 9.0 g of Na(dedtc) in 300 ml of methanol was added to the Nb-SCN solution. The reaction mixture turned yellow-orange. Well-shaped yellow-orange needle crystals formed after 8–12 hr and were filtered and dried under vacuum. The compound can be recrystallized in small batches from large volumes of CCl<sub>4</sub>. However the analysis is not improved by the recrystallization. The initial product is found to give excellent analysis.

**TaCl(OCH<sub>3</sub>)<sub>2</sub>(dedtc)<sub>2</sub>.**—A 6-g sample of TaCl<sub>5</sub> (0.017 mol) was weighed out in a drybox into a 250-ml round-bottom flask fitted with an addition funnel. This apparatus was removed from the drybox. Methanol (50 ml) was added through the funnel. Evolution of HCl resulted. The ligand Na(dedtc)·3H<sub>2</sub>O (7.8 g, 0.035 mol) was dissolved in 100 ml of methanol and this solution was added to the niobium solution; the resulting solution turned pale yellow and there was rapid formation of a white crystalline precipitate. The precipitate was filtered and dried under vacuum. Halide analysis showed a high concentration of NaCl. The compound was purified by recrystallization from CCl<sub>4</sub> in which the NaCl contaminant is insoluble.

**TaBr(OCH<sub>3</sub>)<sub>2</sub>(dedtc)<sub>2</sub>.**—This compound was prepared by the method described for the chloro compound using one-third the total volume of methanol (50 ml). The reaction mixture turned pale green. After 20 min a yellow precipitate formed. This was filtered and dried and subsequently recrystallized from CCl<sub>4</sub> as a white crystalline product. This procedure worked on two occasions. Several similar attempts failed and a reproducible procedure was not developed.

**NbCl(OCH<sub>3</sub>)<sub>2</sub>(dmdtc)<sub>2</sub>.**—A method similar to that used for NbCl(OCH<sub>3</sub>)<sub>2</sub>(dedtc)<sub>2</sub> was employed. When the solution of the ligand was added to the solution of NbCl<sub>5</sub> in methanol, an immediate precipitate of crystalline white flakes formed. The solution did not change color and no further precipitate formed. The solution was allowed to stand for 18–24 hr. The compound could not be recrystallized from CCl<sub>4</sub> since it was insoluble.

**NbBr(OCH<sub>3</sub>)<sub>2</sub>(dmdtc)<sub>2</sub>.**—The procedure used for the chloride compound was successful. The compound was isolated as a pale yellow, flaky, crystalline product. No satisfactory method of recrystallization was found, but the initial product was found to be reasonably pure.

**TaCl(OCH<sub>3</sub>)<sub>2</sub>(dmdtc)<sub>2</sub>.**—This compound was prepared by the same procedure as TaBr(OCH<sub>3</sub>)<sub>2</sub>(dedtc)<sub>2</sub>. The solution turned bright yellow upon addition of the ligand solution. A white

precipitate rapidly formed. This was filtered off and dried under vacuum. The compound was not sufficiently soluble in CCl<sub>4</sub> to allow recrystallization from this solvent. Halide and metal analyses on the crude product indicated that it was contaminated with dimethylammonium chloride.

**NbCl(OCH<sub>3</sub>)<sub>2</sub>(dbdtc)<sub>2</sub>.**—A 5.5-g sample of NbCl<sub>5</sub> (0.02 mol) was dissolved in 100 ml of methanol. This solution was then added to a flask containing 24 g of solid Zn(dbdtc)<sub>2</sub> (0.04 mol). The zinc compound is a white insoluble powder. There was no immediate reaction. The solution, originally clear and colorless, became dark orange after 14 hr. After another 10–12 hr, the solution became bright yellow and the solid turned dark brown. The solid was removed by filtration, dried under vacuum, and recrystallized from CCl<sub>4</sub>. The recrystallized compound is a white crystalline compound and was dried under vacuum.

**NbBr(OCH<sub>3</sub>)<sub>2</sub>(dbdtc)<sub>2</sub>.**—This compound is prepared in the same way as the chloro derivative. The product is a white crystalline compound.

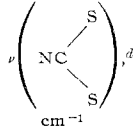
**Use of Other Alcohols.**—Other alcohols have been tried as solvents in order to synthesize compounds with alkoxy groups other than OCH<sub>3</sub>. These attempts met with no success. The addition of an alcohol solution of the ligand to the solution of the metal pentahalide produced immediate precipitation of yellow-white products which did not react further or dissolve on standing or heating. On isolation and drying, they had high metal analyses. Ethyl, *t*-butyl, and *n*-amyl alcohols were used. To counteract the smaller polarity of these alcohols, solvents such as nitromethane were added to some reaction mixtures. This approach was not successful.

### Characterization

**Analysis.**—Analyses, molecular weight data, melting points, and yields of the compounds prepared are presented in Table I. The compounds melt sharply at the temperature indicated except for the dmdtc compounds which char at temperatures around 300°. The compounds are all diamagnetic.

**Conductivities.**—Conductivities were measured in acetonitrile and in methanol and are presented in Table II. The compounds gave values in acetonitrile corresponding to nonelectrolytes. (A 1:1 electrolyte in CH<sub>3</sub>CN has a conductivity of 180–200 mhos.) In

TABLE II  
 MOLAR CONDUCTIVITIES ( $\Lambda_m$ ) AND ULTRAVIOLET AND INFRARED SPECTRAL DATA

Compound	$\Lambda_m(\text{CH}_3\text{CN})^a, \Lambda_0(\text{CH}_3\text{OH})^b$		$T, ^\circ\text{C}$ hr	$\lambda_{\text{max}},$ nm	$10^{-4}\epsilon$	$\nu(\text{CN}),$ $\text{cm}^{-1}$		$\nu(\text{OCH}_3)^d,$ $\text{cm}^{-1}$
	$\text{ohm}^{-1}$ $\text{cm}^2$ $\text{mol}^{-1}$	$\text{ohm}^{-1}$ $\text{cm}^2$ $\text{mol}^{-1}$						
$\text{NbCl}(\text{OCH}_3)_2(\text{dmdtc})_2$	12	40	10	260	10	1528	1140, 1185 w, 1235	1050 sh, 1090
$\text{NbBr}(\text{OCH}_3)_2(\text{dmdtc})_2$	14	45	10	260	8	1530	1140, 1185 w, 1235	1045 sh, 1095
$\text{NbCl}(\text{OCH}_3)_2(\text{dedtc})_2$	15	35	12	260	6	1510	1140, 1185 sh, 1200, 1268	1065, 1090
$\text{NbBr}(\text{OCH}_3)_2(\text{dedtc})_2$	15	40	10	260	8	1510	1135, 1185 sh, 1200, 1270	1067, 1090
$\text{NbNCS}(\text{OCH}_3)_2(\text{dedtc})_2$	9	9	15	255	7	1510	1142, 1190 sh, 1200, 1270	1070 sh, 1082
$\text{TaCl}(\text{OCH}_3)_2(\text{dedtc})_2$	20	25	1	260	2.4	1515	1145, 1185 sh, 1200, 1270	1065, 1095
$\text{TaBr}(\text{OCH}_3)_2(\text{dedtc})_2$	24	30	1	...	...	1512	1145, 1190 sh, 1201, 1272	1067, 1090
$\text{NbCl}(\text{OCH}_3)_2(\text{dbdte})_2$	16	30	20	265	7	1485	1148, 1218, 1255, 1270	1075 sh, 1095
$\text{NbBr}(\text{OCH}_3)_2(\text{dbdte})_2$	15	30	20	265	6	1485	1140, 1210, 1250, 1265	1070 sh, 1082

<sup>a</sup> Conductivity studies used  $1.0 \times 10^{-3} M$  solutions. <sup>b</sup>  $\Lambda_0$  is the molar conductivity of a fresh solution a few minutes after preparation. <sup>c</sup>  $T$  is the number of hours until the conductivity corresponded to  $120 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  which corresponds to a 1:1 electrolyte. <sup>d</sup> Abbreviations: sh, shoulder; w, weak.

methanol the initial values indicate nonelectrolyte behavior. The conductivity of these solutions increased with time. The conductivity of the solutions of the tantalum(V) compounds increased much more rapidly than that of the niobium compounds. This may explain the difficulty in preparing the tantalum compounds.

**Electronic Spectra.**—Table II shows the wavelengths of maximum absorption in the ultraviolet and the corresponding molar absorptivities ( $\epsilon$ ) for the compounds studied. The compounds exhibit a single, fairly broad maximum whereas the free carbamate anions exhibit two maxima: one at 250 nm ( $\epsilon$  12,000) and another at 280–300 nm ( $\epsilon$  13,000).<sup>4</sup> The spectra are stable with time in acetonitrile but change in methanol to give initially the spectra of the parent carbamate anion. These spectra further change to a flat base line. During the early stages of decomposition in methanol the solutions become yellow due to the development of a weak maximum at 435 nm ( $\epsilon$  50). This color fades at a later stage of decomposition.

Similar spectral changes occur in solutions of other primary and secondary alcohols. Stable spectra similar to those in acetonitrile are observed in *t*-butyl alcohol.

**Infrared Spectra.**—Table II shows infrared bands of the prepared complexes. The intense band in the  $1500\text{-cm}^{-1}$  region is indicative of the  $\text{C}\equiv\text{N}$  bond of the carbamate ligand. The carbamate ligands in our compounds are coordinated through the S atoms. If there were MN bonds present, the  $\text{C}\equiv\text{N}$  bond would appear at much lower frequencies. The  $\text{C}\equiv\text{N}$  bond, especially upon coordination of the carbamate ligand, is intermediate between a double bond and a single bond.<sup>5,6</sup> The frequency of the  $\text{C}\equiv\text{N}$  band decreases with increasing length of the alkyl chain bonded to the nitrogen. This fact has been previously noted by McCormick in carbamate complexes of oxovanadium(IV).<sup>7</sup>

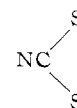
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The three bands in the  $1130\text{--}1290\text{-cm}^{-1}$  region are associated with the



grouping.<sup>8</sup> The pattern observed in all compounds is that expected for carbamates coordinated through two sulfur atoms. A more complex pattern has been reported for a molecule containing a "dangling" carbamate ligand.<sup>9</sup> Also shown in the table is the band for the CO stretch of the coordinated methoxy group.<sup>10</sup>

Infrared data were also used to determine the linkage of the thiocyanate ion in  $\text{NbNCS}(\text{OCH}_3)_2(\text{dedtc})_2$ . Pecile<sup>11</sup> has demonstrated that for planar and tetrahedral thiocyanate complexes, the integrated intensity,  $A$  ( $M^{-1} \text{ cm}^{-2}$ ), of the CN asymmetric stretch band at about  $2100 \text{ cm}^{-1}$  has a value of  $(0.8\text{--}2.3) \times 10^4 M^{-1} \text{ cm}^{-2}$  for S-bonded thiocyanate and  $(9\text{--}12) \times 10^4$  for N-bonded thiocyanate. (These values are relative to a value of approximately  $4.5 \times 10^4$  for free thiocyanate.) In general it has been observed<sup>12</sup> that the integrated intensity of the CN band for N-bonded thiocyanate complexes is greater than for unbound  $\text{SCN}^-$ ; the intensity in S-bonded complexes is less than for free thiocyanate ion. Integrated intensity measurements of the CN band which appears at approximately  $2080 \text{ cm}^{-1}$  were made using several concentrations of compound. We obtained an average value of  $21 \times 10^4 M^{-1} \text{ cm}^{-2}$  relative to a measured value for free thiocyanate of  $4.5 \times 10^4 M^{-1} \text{ cm}^{-2}$ . This evidence indicates N-bonded thiocyanate in  $\text{NbNCS}(\text{OCH}_3)_2(\text{dedtc})_2$ . The above study was necessitated since the CS region in the infrared contains bands due to both NCS and the carbamate ligands. Recent work by Knox and Brown<sup>13</sup> used infrared studies to assign Nb–NCS bonding in  $\text{Nb}(\text{NCS})_6^-$ .

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TABLE III  
NMR DATA

Compound	Freq <sup>a</sup>	Assignment
NbCl(OCH <sub>3</sub> ) <sub>2</sub> (dmdtc) <sub>2</sub>	78	CH <sub>3</sub>
	226	OCH <sub>3</sub>
NbBr(OCH <sub>3</sub> ) <sub>2</sub> (dmdtc) <sub>2</sub>	78	CH <sub>3</sub>
	226	OCH <sub>3</sub>
Na(dedtc)	70 t	CH <sub>3</sub>
	242 q	CH <sub>2</sub>
NbCl(OCH <sub>3</sub> ) <sub>2</sub> (dedtc) <sub>2</sub>	77 t	CH <sub>3</sub>
	232 q	CH <sub>2</sub>
	229	OCH <sub>3</sub>
NbBr(OCH <sub>3</sub> ) <sub>2</sub> (dedtc) <sub>2</sub>	80 t	CH <sub>3</sub>
	234 o	CH <sub>2</sub>
	230	OCH <sub>3</sub>
NbNCS(OCH <sub>3</sub> ) <sub>2</sub> (dedtc) <sub>2</sub>	79 t	CH <sub>3</sub>
	232 q	CH <sub>2</sub>
	240	OCH <sub>3</sub>
Na(dbdtc)	320	CH <sub>2</sub>
	436	C <sub>6</sub> H <sub>5</sub>
Zn(dbdtc) <sub>2</sub>	304	CH <sub>2</sub>
	442	C <sub>6</sub> H <sub>5</sub>
NbCl(OCH <sub>3</sub> ) <sub>2</sub> (dbdtc) <sub>2</sub>	243	OCH <sub>3</sub>
	295	CH <sub>2</sub>
	439	C <sub>6</sub> H <sub>5</sub>
NbBr(OCH <sub>3</sub> ) <sub>2</sub> (dbdtc) <sub>2</sub>	243	OCH <sub>3</sub>
	296	CH <sub>2</sub>
	439	C <sub>6</sub> H <sub>5</sub>
TaCl(OCH <sub>3</sub> ) <sub>2</sub> (dedtc) <sub>2</sub>	80 t	CH <sub>3</sub>
	230 q	CH <sub>2</sub>
	248	OCH <sub>3</sub>
TaBr(OCH <sub>3</sub> ) <sub>2</sub> (dedtc) <sub>2</sub>	82 t	CH <sub>3</sub>
	228 o	CH <sub>2</sub>
	250	OCH <sub>3</sub>

<sup>a</sup> Frequency of line or center of multiplet in hertz at 60 MHz. Tetramethylsilane (TMS) was the internal standard. Abbreviations: t, triplet; q, quartet; o, octet. All triplets and quartets showed a splitting of 7 Hz. The octets were composed of a quartet with a splitting of 7 Hz in which each resonance was split into a doublet with a splitting of 2 Hz.

**Proton Nuclear Magnetic Resonance Spectra.**—Table III presents proton magnetic resonance data on the compounds prepared and some carbamate salts. A spectrum of (H<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>)(CH<sub>3</sub>)<sub>2</sub>NCS<sub>2</sub> could not be obtained since it was not sufficiently soluble in the solvents used (CDCl<sub>3</sub> and CD<sub>3</sub>CN). The spectra and their integration were consistent with the proposed stoichiometries of the compounds. Sufficiently large shifts in the resonances of the N-alkyl groups occur on coordination of the carbamates to permit one to distinguish between free and coordinated ligands.

The quartet expected for CH<sub>2</sub> (split by CH<sub>3</sub>) in MBr(OCH<sub>3</sub>)<sub>2</sub>(dedtc)<sub>2</sub> appears as two overlapping equal-intensity quartets shifted from one another by 2 Hz. The CH<sub>3</sub> triplet is broad. (The probe temperature in our instrument is about 37°.) At lower temperatures the triplet resolves into two overlapping triplets. The corresponding chloro compounds give a single quartet at 37°, but as the temperature is lowered, the quartet and the triplet resolve in a manner similar to the bromo compounds. The overlapping CH<sub>2</sub> quartets and CH<sub>3</sub> triplets indicate the presence of nonequivalent ethyl groups. An explanation which is consistent with the observations recognizes restricted rotation about the C—N

bond. The rotational barrier can be postulated to be of such magnitude in the bromo derivative that the rate of rotation is sufficiently slow at 37° that the two ethyl groups on one carbamate nitrogen see different environments during the nmr experiment. The fact that the overlapping multiplets are not resolved in the chloro compounds at 37° suggests that the rotational barriers are smaller in these molecules. This could result from the smaller size of the chloro group which might permit easier rotation or from its smaller π-acceptor ability which could lower the double-bond character in the C=N bond. It seems less likely that this type of temperature behavior would be observed as a result of nonequivalent carbamate ligands. The nature and temperature dependence of the CH<sub>2</sub>CH<sub>3</sub> spectrum is added evidence that the carbamate ligands are coordinated in a bidentate manner through sulfur atoms. It is hard to visualize how a molecule containing either one or two "dangling" carbamate ligands could produce the observed spectra.

Several substitution reactions were attempted and were monitored using nmr. Methoxide exchange with NbCl(OCH<sub>3</sub>)<sub>2</sub>(dedtc)<sub>2</sub> was tried using a 2:1 ratio of CH<sub>3</sub>OH to complex in CD<sub>3</sub>CN. No broadening or shift in free or coordinated OCH<sub>3</sub> resonance was observed. Related studies using ethanol or *t*-butyl alcohol in place of methanol provided no evidence for interchange.

Exchange and interchange studies involving the carbamate ligands were also attempted. A solution containing a 2:1 ratio of Na(dedtc) to NbCl(OCH<sub>3</sub>)<sub>2</sub>(dedtc)<sub>2</sub> in CD<sub>3</sub>CN had a spectrum which remained unchanged for 24 hr and was the sum of the spectra of the separate compounds. There was also no apparent reaction in a similar study of Na(dbdtc) and NbCl(OCH<sub>3</sub>)<sub>2</sub>(dbdtc)<sub>2</sub>.

When solutions of Na(dbdtc) and NbCl(OCH<sub>3</sub>)<sub>2</sub>(dedtc)<sub>2</sub> (2:1) were mixed in CD<sub>3</sub>CN, nmr spectral changes occurred which were complete in 24 hr. The bands corresponding to coordinated dedtc were unchanged but the CH<sub>2</sub> resonance of the dbdtc shifted from 323 to 302 Hz, which corresponds to coordination of this ligand. (TMS was used throughout as the reference.) The OCH<sub>3</sub> resonance shifted from 238 to 210 Hz which may indicate displacement of OCH<sub>3</sub>. The related reaction between Na(dedtc) and NbCl(OCH<sub>3</sub>)<sub>2</sub>(dbdtc)<sub>2</sub> (2:1) was also run. In 18 hr there was a complete shift of the free dedtc resonance to a position corresponding to coordinated ligand. The dbdtc resonance shifted from 300 to 322 Hz which corresponds to its conversion to free ligand. The OCH<sub>3</sub> resonance shifted to 196 Hz. These data suggest that dedtc forms a more stable complex than dbdtc and will slowly displace the latter. It also suggests that in these mixed systems more than two carbamate ligands are coordinated with a corresponding displacement of OCH<sub>3</sub>. Attempts to confirm the latter reaction by synthetic studies did not yield pure products.

**Summary of Structural Information.**—The studies discussed in this paper indicate that the compounds

reported are monomers in which the metal is coordinated to seven donor atoms. The nmr studies suggest that the  $\text{OCH}_3$  ligands are probably equivalent. The environments on opposite ends of the essentially planar carbamate ligands seem to be different.

A model which is consistent with these observations and preliminary X-ray data has *trans* axial  $\text{OCH}_3$  groups with the carbamate ligands and the halogen in the equatorial positions of a pentagonal bipyramid. A

single-crystal X-ray study of  $\text{NbBr}(\text{OCH}_3)_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$  is in progress.

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## Complexes of Titanium(IV) Containing the 3-Methyl-2,4-pentanedionate Anion

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Seven 3-methyl-2,4-pentanedionate complexes of titanium(IV) have been prepared and characterized. These include  $\text{X}_2\text{Ti}(\text{C}_6\text{H}_9\text{O}_2)_2$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ),  $\text{X}_3\text{Ti}(\text{C}_6\text{H}_9\text{O}_2)$  ( $\text{X} = \text{Cl}, \text{Br}$ ), and  $[\text{Ti}(\text{C}_6\text{H}_9\text{O}_2)_3]\text{Y}$  ( $\text{Y}^- = \text{FeCl}_4^-, \text{SbCl}_6^-$ ). The dihalo and trihalo complexes are monomeric and nonionic; the trisubstituted complexes are 1:1 electrolytes. Nmr data show that the dihalo complexes have the *cis* configuration.

### Introduction

The past few years have seen an interest in the reactions of titanium tetrahalides with  $\beta$ -diketones.<sup>2–7</sup> Complexes most frequently isolated are (1) simple Lewis acid–base adducts of the  $\beta$ -diketones, (2) mono-substituted  $\text{X}_3\text{TiL}$  enolate complexes, and (3) disubstituted  $\text{X}_2\text{TiL}_2$  complexes. Further, tris-substituted complexes containing an  $\text{L}_3\text{Ti}^+$  cation have been isolated mainly by the reaction of  $\text{Cl}_2\text{TiL}_2$  complexes with a suitable Lewis acid such as antimony pentachloride or ferric chloride. In this paper we report the preparation and characterization of titanium(IV) complexes containing the 3-methyl-2,4-pentanedionate anion.

### Experimental Section

**Reagents.**—Titanium tetrafluoride, titanium tetrabromide (Alfa Inorganics, Inc.), and titanium tetrachloride (Fisher Scientific Co., "purified") were purchased. Titanium tetrachloride was redistilled under nitrogen just prior to use; the other tetrahalides were used without further purification. 3-Methyl-2,4-pentanedione was prepared and characterized by a reported procedure.<sup>2d,5</sup>

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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.<sup>4b</sup>

**General Procedures.**—All preparations were performed under an atmosphere of dry nitrogen by methods previously described.<sup>2d</sup> All compounds were washed thoroughly with hexane and dried under vacuum at room temperature. Physical measurements were made on samples prepared in a nitrogen-filled glove bag or a Vacuum Atmospheres Dri-Lab.

**Preparation of Trichloro(3-methyl-2,4-pentanedionato)titanium(IV).**—3-Methyl-2,4-pentanedione ( $2.5 \times 10^{-2}$  mol) in methylene chloride (15 ml) was added dropwise to a solution of titanium tetrachloride ( $2.7 \times 10^{-2}$  mol) in 40 ml of methylene chloride. A dark solution resulted. Approximately half the methylene chloride was boiled off under a slow stream of nitrogen. Hexane was then added; a dark red precipitate formed and was subsequently isolated. *Anal.* Calcd for  $\text{C}_6\text{H}_9\text{O}_2\text{Cl}_3\text{Ti}$ : C, 26.94; H, 3.40; Cl, 39.8. Found: C, 26.51; H, 3.58; Cl, 38.6.

**Preparation of Tribromo(3-methyl-2,4-pentanedionato)titanium(IV).**—This complex was prepared like trichloro(3-methyl-2,4-pentanedionato)titanium(IV). A dark crystalline solid was isolated. This complex was extremely moisture sensitive showing immediate decomposition on contact with air. *Anal.* Calcd for  $\text{C}_6\text{H}_9\text{O}_2\text{Br}_3\text{Ti}$ : C, 17.98; H, 2.26; Br, 59.8. Found: C, 17.99; H, 2.51; Br, 58.5.

**Preparation of Difluorobis(3-methyl-2,4-pentanedionato)titanium(IV).**—Titanium tetrafluoride ( $1.18 \times 10^{-2}$  mol) was added to 20 ml of methylene chloride. 3-Methyl-2,4-pentanedione ( $2.23 \times 10^{-2}$  mol) was added dropwise to the slurry. The reaction mixture was refluxed 4 hr. Hexane was then added, after which the methylene chloride was gently boiled off; an oil remained. Addition of dried ether with stirring gave a yellow precipitate. *Anal.* Calcd for  $\text{C}_{12}\text{H}_{18}\text{O}_4\text{F}_2\text{Ti}$ : C, 46.17; H, 5.81. Found: C, 46.30; H, 5.93.

**Preparation of Dichlorobis(3-methyl-2,4-pentanedionato)titanium(IV).**—This complex was prepared by a procedure similar to that reported by Fay and Lowry.<sup>4b</sup> A red-orange precipitate was