

유기-티탄 화학 (제 1 보). Dichlorodicarboxylatotitanium(IV)의 합성 및 분자구조

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Organotitanium Chemistry I (I). Synthesis and Molecular Structure of Dichlorodicarboxylatotitanium(IV)

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요 약 : 사염화 티탄과 초산, 프로피온산, 크로톤산, 벤조산, 휴로산, 살리실산 등을 디클로로메탄 용매속에서 반응시켜 결정성 화합물을 얻었다. 화학분석을 해본 결과 이들은 모두 이클로로비스카르복실아토티탄(IV) 즉 $TiCl_2(OOCR)_2$ 임을 알수 있었으며 이클로로비스프로피온아토티탄(IV)의 분자량 측정결과 이합체임을 알았다. 이 화합물들의 적외선 스펙트럼을 보면 진부 $1500-1700cm^{-1}$ 근처에서 카르본일기의 비대칭 신축 진동을 나타내는 밴드가 두개씩 나타났으며 이클로로비스프로피온아토티탄(IV)의 핵자기공명 스펙트럼에도 메칠피크와 메칠렌 피크가 각각 두개씩 나타나는 것으로 보아 이합체인 $(TiCl_2(OOCR)_2)_2$ 중의 두개의 카르복실산기는 다른 두개의 카르복실산기와 화학적으로 동등하지 않음을 알 수 있었다. 따라서 이들의 분자구조로써 두개의 카르복실산기가 두 티탄 원자의 다리역활을 하는 이합체의 구조를 제안하였다.

Abstract. Crystalline products were obtained when $TiCl_4$ was reacted in dichloromethane with acetic, propionic, crotonic, benzoic, furoic and salicylic acids. Chemical analysis has shown that these were all dichlorodicarboxylatotitanium(IV). Cryoscopy of dichlorodipropionatotitanium(IV) indicated the carboxylato-complexes are dimeric. In the IR spectra of these complexes two strong bands both assigned to asymmetric carbonyl stretching vibration have been observed in the region $1500-1700cm^{-1}$ and the NMR spectrum of dichlorodipropionatotitanium(IV) has also shown two triplets and two quartets, which indicate that there are two chemically unequivalent carboxylato-ligands in the dimer $[TiCl_2(OOCR)_2]_2$. Their molecular structure was proposed to be bis-carboxo-bridged dimer.

Introduction

Titanium is one of the most reactive transition metals toward organic compounds to form

organotitanium complexes.¹ Unfortunately, the increasing interest in this field is frustrated by the fact that most organotitanium compounds are extremely moisture sensitive. Nevertheless, the alkoxytitanium complexes, particularly,

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tetraalkoxytitanium^{2,3} $(RO)_4Ti$ have been extensively studied because of their wide applicability to industrial uses. However, carboxylato-titanium complexes have yet received a systematic study.

Prasad and Srivastava⁴, Jacini⁵, and Plechner and Ryan⁶ claimed the preparation of several tetracarboxylatotitanium from reaction of titanium tetrahalide and excess organic acids, but their existence was questioned by other workers⁷⁻⁹. In general, the reaction of titanium tetrahalide and carboxylic acids leads to the formation of halogenotitanium carboxylates having the general formula $(RCOO)_nTiCl_{4-n}$. No report is available on the synthesis of such halogeno-complexes of a definite composition except for dichlorodiacetatotitanium (IV) $(TiCl_2(OAc)_2)^{10-12}$ and dichlorodipropionatotitanium (IV)⁷. Furthermore, structural study on carboxylato-complexes are not available at all. In this work we attempted reactions of titanium tetrachloride with various organic acids in inert organic solvents and have succeeded in isolation of several dichlorodicarboxylato-complexes in crystalline state. Their molecular structure could be elucidated from infrared and NMR spectra and cryoscopic data.

Experimental

All reactions and measurements were carried out in thoroughly dried state under inert atmosphere, since organotitanium compounds are extremely moisture sensitive.

Apparatus and Equipments. An air-tight dry box and specially designed glass equipments were employed for safe operation. Chemical reactions were performed in the dry box using a two-necked flask to which a pressure-equilibrated funnel was ground-jointed. One of the reactants was added through this funnel. Such reaction glass unit was designed so that its

inner atmosphere may be isolated from that of the dry box and also be purged with dry nitrogen as is seen in Fig. 1. A special filtering unit was built (shown in the Fig. 1) for filtration of compounds under vacuum or pressure. Glasswares were always washed finally with dry acetone and then vacuum dried before use.

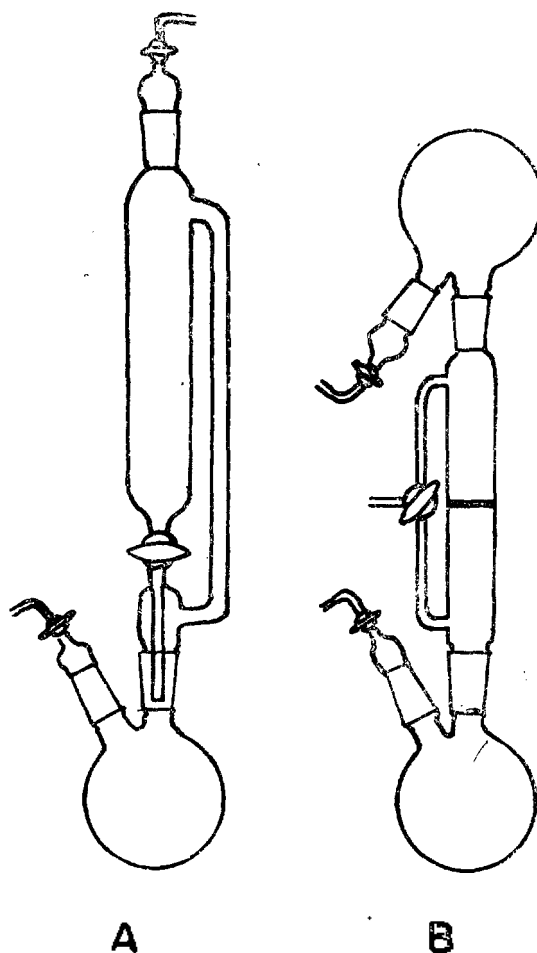


Fig. 1. A, Reaction system; B, Filtering unit

Chemicals and Purifications. Nitrogen was purified by passing it through columns of heated copper and anhydrous calcium sulfate. Solvents used for chemical reactions were reagent grade dichloromethane, *n*-hexane and benzene. These were refluxed with calcium

hydride for 24 hours and then fractionally distilled under exclusion of moisture. The carboxylic acids were also all reagent grade and dried before use. Reagent grade titanium tetrachloride (Wako) was used without further purification.

Compound Preparations. Dichlorodiacetatotitanium (IV). — 10 *m* mole of titanium tetrachloride in dichloromethane was slowly added to acetic acid (20 *m* mole) in the same solvent. The reaction system was purged with a slow stream of nitrogen to remove evolving hydrogen chloride. Light yellow crystals were formed. m. p. 120–125 °C of $\text{TiCl}_2(\text{CH}_3\text{COO})_2$. Found: Ti, 20.0; Cl, 28.6. Calc.: Ti, 20.2; Cl, 29.9.

Dichlorodipropionatotitanium (IV). — TiCl_4 (10 *m* mole) in dichloromethane was added to propionic acid (20 *m* mole) in the same solvent under nitrogen stream. The reaction mixture was refluxed for 10 min. After cooling *n*-hexane was slowly added until precipitation started. On standing was formed a light yellow crystalline product which was recrystallized twice in CH_2Cl_2 -*n*-hexane solvent pair. m. p. 75 °C decomp. Chem. Anal. of $\text{TiCl}_2(\text{C}_2\text{H}_5\text{COO})_2$. Found: Ti, 18.1; Cl, 25.3; Calc.: Ti, 18.1; Cl, 26.7.

Dichlorodicrotonatotitanium (IV), Dichlorodibenzoatotitanium (IV) and Dichlorodifuroatotitanium (IV). — These compounds were prepared in the same way as in the above. But the benzoato- and furoato-complexes could not be recrystallized because of low solubility in organic solvents and attempted recrystallization of $\text{TiCl}_2(\text{CH}_3\text{CH}=\text{CHCOO})_2$ yielded oily product. $\text{TiCl}_2(\text{CH}_3\text{CH}=\text{CHCOO})_2$. m. p. 116 °C, Found: Ti, 16.9; Cl, 18.9; C, 34.2. Calc.: Ti, 16.7; Cl, 24.7; C, 33.5. $\text{TiCl}_2(\text{C}_6\text{H}_5\text{COO})_2$. m. p. 139 °C decomp. Found: Ti, 13.4; Cl, 16.5; C, 45.9. Calc.: Ti, 13.2; Cl, 19.5; C,

46.3. $\text{TiCl}_2(\text{C}_6\text{H}_5\text{OCOO})_2$. m. p. 160 °C decomp. Found: Ti, 13.5; Cl, 18.9; C, 35.2. Calc.: Ti 14.1; Cl, 20.9; C, 35.2.

Dichlorodisalicylatotitanium (IV). — Salicylic acid (20 *m* mole) and TiCl_4 (10 *m* mole) in benzene were mixed. Purple crystals were formed. m. p. >400 °C. Chem. Anal. of $\text{TiCl}_2(\text{Sal.})_2$. Found: Ti, 11.8; Cl, 18.0; C, 42.8. Calc.: Ti, 12.2; Cl, 18.0; C, 42.8.

Physical Measurements. Infrared spectra of the compounds were measured in nujol mull using Beckman Model 12 Infrared Spectrophotometer. NMR spectra of dichlorodipropionatotitanium (IV) in dichloromethane were recorded on a Varian Model HA-100 D Spectrometer and the sample temperature was controlled by means of a Varian Model V-6040 Variable Temperature Controller and liquid nitrogen. The molecular weight of the propionato-complex was measured cryoscopically in dry benzene by employing specially designed thermistor thermometer unit¹³. All samplings were performed in the dry box.

Chemical Analysis. Titanium was determined gravimetrically as TiO_2 . Chloride ion was precipitated with excess AgNO_3 solution and then the excess silver was titrated with the standard potassium thiocyanate solution. Carbon and hydrogen were determined using Coleman Model 33 C-H Analyzer.

Results and Discussion

Crystalline products were obtained when titanium tetrachloride was reacted with acetic and propionic acids whereas with higher boiling acids resulted oily materials except with crotonic acid. Aromatic acids also led to formation of crystalline solids. Chemical analysis has shown that all these carboxylato-complexes are dichlorodicarboxylatotitanium (IV) having the general formula $\text{TiCl}_2(\text{OOCR})_2$. The organic

ligands were further confirmed by carbon analysis and infrared spectra which will be discussed later. Experimental values of chlorine analysis are always lower than the calculated probably because of its loss during sample dissolution process. In fact, hydrogen chloride could be detected during the procedure.

All the dicarboxylato-complexes are extremely sensitive to moisture and rapidly hydrolyzed in the air. Propionato- and crotonato-complexes are soluble in polar and aromatic solvents, but the other salts are only slightly soluble or insoluble in organic solvents except in alcohols in which they dissolve by solvolytic reaction¹⁴.

Attempts to prepare tri- or tetracarboxylato-complexes by varying the mole ratio of the reactants in the same solvent have failed and ended up with production of only dicarboxylato-complexes. Changing the solvent resulted in the same. For instance, when TiCl_4 was reacted with benzoic or salicylic acid in ethyl ether solvated dichlorodicarboxylatotitanium (IV) $\text{TiCl}_2(\text{OOCR})_2 \cdot n\text{Et}_2\text{O}$ were obtained. More vigorous temperature condition seems to be necessary for replacement of more than two chlorine atoms. Although some tetra-substituted complexes in which the ligand is a long-chained aliphatic or aromatic carboxy group were claimed⁴⁻⁶, no reproduction was reported. Furthermore other numerous attempts¹⁵ to prepare tetraacetatotitanium (IV) have not been successful. At any rate it seems that the activation energy to eliminate from titanium more than two chlorine atoms is very high.

The molecular structure of organotitanium compounds has been very little reported. As far as the crystal structure is concerned, no study has been made on alkoxy or carboxylato-titanium complexes probably because of their instability. As a result, coordination chemistry of titanium complexes was not well established,

despite that a great number of compounds were prepared. The coordination number¹⁶ of Ti-complexes is known to be any from 4 to 8 for which examples are all known, but 6-coordination is most common in organotitanium complexes. In this paper will be illustrated that the molecular structure of dichlorodicarboxylatotitanium (IV) may be deduced from their infrared and NMR spectra and cryoscopic data.

The molecular weight of soluble dichlorodipropionatotitanium (IV) determined cryoscopically in benzene was found to be 540, which is about double of the calculated value (256). This means the propionato-complex is dimeric and the dimer is probably carboxo or chlorobridged. The chemically feasible molecular structure according to the above cryoscopic data would be the following: $(\text{RCOO})_2\text{Ti}(-\text{Cl}-)_4\text{Ti}(\text{OOCR})_2$ (I), $\text{Cl}_2\text{Ti}(-\text{O}-\underset{\text{R}}{\text{C}}-\text{O}-)_4\text{TiCl}_2$ (II), $\text{Cl}_2(\text{RCOO})-\text{Ti}(-\text{O}-\underset{\text{R}}{\text{C}}-\text{O}-)_2\text{Ti}(\text{OOCR})\text{Cl}_2$ (III). In each of these structures the titanium metal is 6-coordinated. It will be next shown that the structure (I) and (II) may be excluded by consideration of their IR and NMR spectra.

The infrared spectrum of the propionato-complex is shown in Fig. 2 and also the spectra of other salts are tabulated in Table 1. It is common in the dicarboxylato-complexes that a few additional bands appear in the low frequency range ($500-700\text{ cm}^{-1}$) besides the absorption bands by the free acids. Since Ti-Cl stretching frequency¹⁷ is generally less than 500 cm^{-1} , the low energy bands (e. g. 580 and 733 cm^{-1} bands in $\text{TiCl}_2(\text{OOC}_2\text{H}_5)_2$, are good candidates for the stretching vibration of Ti-O bonds newly formed by coordination of propionato-ligand to the metal. Further study is necessary for more definite assignment of these bands. More important is that two strong bands were observed in the carbonyl stretching region

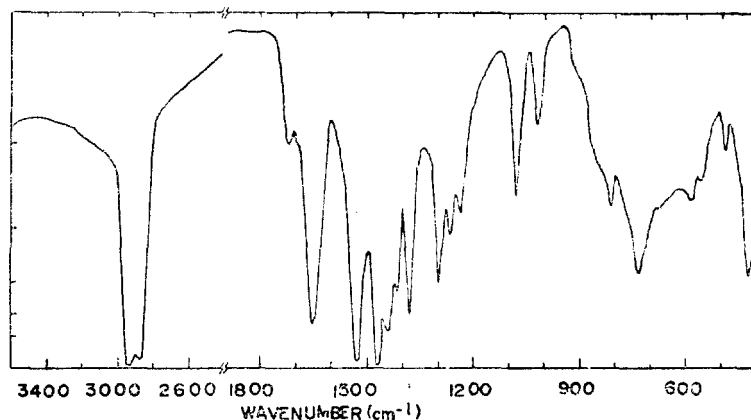


Fig. 2. Infrared spectrum of dichlorodipropionatotitanium(IV) in nujol mull.

Table 1. Infrared Spectra of $\text{TiCl}_2(\text{OOCR})_2^*$

$\text{TiCl}_2(\text{Ac})_2$: 563 (M), 612 (M), 653 (M), 675 (W), 740 (M), 912 (W), 960 (W), 1029 (M), 1046 (M), 1245 (M), 1555 (M), 1662 (S),
$\text{TiCl}_2(\text{Pr})_2$: 485 (W), 580 (W), 733 (S), 810 (W), 1018 (M), 1080 (S), 1240 (M), 1270 (M), 1303 (M), 1410 (W), 1440 (W), 1530 (S), 1655 (S), 1720 (W),
$\text{TiCl}_2(\text{Cr})_2$: 475 (S), 528 (M), 580 (M), 680 (S), 725 (S), 850 (M), 921 (M), 968 (S), 1028 (M), 1110 (M), 1255 (S), 1300 (M), 1575 (M), 1655 (S),
$\text{TiCl}_2(\text{Bz})_2$: 500 (S), 590 (M), 670 (M), 680 (M), 720 (S), 850 (W), 940 (W), 1025 (W), 1070 (W) 1110 (W), 1160 (M), 1178 (M), 1250 (W), 1315 (Sh), 1415 (W), 1500 (W), 1570 (W), 1600 (S), 1645 (S), 1700 (W),
$\text{TiCl}_2(\text{Fur})_2$: 515 (S), 590 (W), 615 (W), 725 (Sh), 750 (S), 770 (Sh), 885 (M), 938 (M), 1020 (M), 1080 (M), 1125 (M), 1135 (M), 1210 (S), 1235 (W), 1415 (W), 1550 (W), 1580 (Sh), 1650 (S),
$\text{TiCl}_2(\text{Sal})_2$: 460 (S), 655 (Sh), 665 (S), 758 (S), 790 (S) 890 (S), 1030 (W), 1093 (M), 1143 (W), 1165 (W), 1210 (M), 1225 (M), 1250 (M), 1268 (Sh), 1425 (M), 1560 (M), 1600 (S)

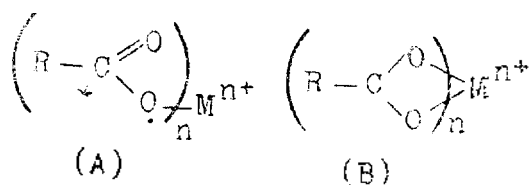
*S, Strong; M, Medium; W, Weak; Sh, Shoulder.

and the both at 1655 and 1530 cm^{-1} in the propionato-complex could be assigned with certainty to the asymmetric carbonyl stretching vibration. The symmetric carbonyl bands corresponding to each of the asymmetric ones

could not be easily identified because of the interference by the strong nujol peaks. In general, a carboxy group RCOO^- shows two carbonyl bands, one by asymmetric carbonyl stretching and the other by symmetric carbonyl stretching vibration. The symmetric carbonyl frequency is never higher than 1500 cm^{-1} .^{18,19}

The above experimental results certainly indicate that the propionato ligands in the complex are not in the same chemical environment.

In other words the four propionato-ligands in the dimeric complex $(\text{TiCl}_2(\text{OOCCH}_2\text{CH}_3)_2)_2$ coordinate to the metal in two different ways. Such conclusion is in accord only with structure (III), since in structures (I) and (II) the carboxylato-ligands are all equivalent. Similarly were observed in the other dicarboxylato-complexes two asymmetric carbonyl bands which were listed in Table 2 and as such their metal-ligand bonding seems to be the same as in the propionato-complex. In general, carboxylato-ligand coordinates to the metal in two different schemes as shown in the following.



In structure (A) the ligand is a monodentate whereas it functions as bidentate in structure (B). Both examples are known^{18,19} but the two different bonding patterns are not sharply distinguished by infrared spectra, since the M—O bond strength rather than the bonding-pattern is frequently more effective on the carbonyl frequency. However, suffice it to say that the carboxylate ion tends to function as bidentate if the central metal attains stable coordination number by such chelation.

The NMR spectra of dichlorodipropionatotitanium (IV) in dichloromethane shown in Fig. 3 are also completely in accord with the structure (III). It is a striking result that the methyl (CH₃—) and methylene (—CH₂—) protons of the propionato-ligand are split into two groups of triplets and quartets, respectively, when the temperature is lowered. Moreover, the integrated

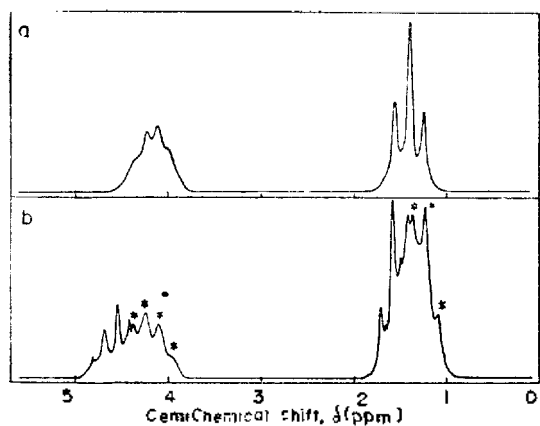


Fig. 3. NMR spectra of dichlorodipropionatotitanium (IV): a. at 30 °C; b. at -67 °C

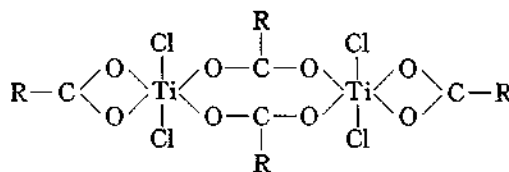
The methyl and methylene proton peaks are each split into two groups marked (*) and unmarked.

areas of the two triplets (or quartets) seem approximately to be equal. Such experimental results clearly indicate that the two propionato-ligands in $[\text{TiCl}_2(\text{OOCCH}_2\text{CH}_3)_2]_2$ are chemically different from the other two. Therefore, it may be concluded that the molecular structure

Table 2. Asymmetric carbonyl stretching frequencies of $\text{TiCl}_2(\text{OOCR})_2$, (cm^{-1})

Compounds	Complex	Free	$\Delta\nu$
$\text{TiCl}_2(\text{Ac})_2$	1,660	1,720	60
	1,555		165
$\text{TiCl}_2(\text{Pr})_2$	1,655	1,720	65
	1,530		190
$\text{TiCl}_2(\text{Cr})_2$	1,655	1,700	45
	1,575		125
$\text{TiCl}_2(\text{Bz})_2$	1,645	1,685	40
	1,600		85
$\text{TiCl}_2(\text{Fur})_2$	1,650	1,685	35
	1,580		105
$\text{TiCl}_2(\text{Sal})_2$	1,600	1,600	60
	1,560		100

of dichlorodipropionatotitanium (IV) is probably the structure (III) as diagrammed in the following. In fact, this structure



seems to be sterically most stable. The other dicarboxylato-complexes are expected to be same except for the salicylato-complex.

In salicylato-complex the possibility of an alternative structure could not be excluded. Chemical analysis has shown that a titanium atom was bonded to two chloride and two salicylate ions. Since salicylic acid has another possible reaction site, that is, an alcohol group in ortho-position to the carboxy group, a strongly bidentated monomeric structure

$\text{H}_2\text{C}(\text{C}_6\text{H}_4\text{COO})_2\text{Ti}_2\text{Cl}_2$ is plausible. A similar type $\text{Ti}(\text{OC}_6\text{H}_5\text{COO})_3^{2-}$ was reported to be formed by reaction of aqueous TiCl_4 and sodium salicylate²⁰. The above ionic form could not be experimentally tested to distinguish from the bridged dimeric structure (III) because the

compound was insoluble in organic solvents. However, it should be noted that the salicylato-complex has shown a considerable difference in physical properties from the other salts. It is themally very stable and least sensitive to moisture.

Acknowledgement

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