

Interaction of TiF_4 with the donor solvents SO_2 , PhCN, and MeCN Isolation and structural characterization of the first trimeric fluorine bridged donor–acceptor adduct $\{\text{TiF}_4(\text{PhCN})\}_3$

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Abstract

There has been speculations on the structures of TiF_4 polymeric complexes $\{\text{TiF}_4\text{L}\}_n$ (L = molecular donor) for several decades, however no structurally characterized examples have been reported. In this work the complex $\{\text{TiF}_4(\text{PhCN})\}_3$ was isolated from a solution of TiF_4 in PhCN (donor number $\text{DN} = 11.9 \text{ kcal mol}^{-1}$) as well as from the mixtures PhCN/ CH_2Cl_2 and PhCN/toluene and characterized by X-ray, IR, NMR, EI-MS. The structure of the complex $\{\text{TiF}_4(\text{PhCN})\}_3$ can be regarded as formed by combining three *face*- $\text{TiF}_3(\text{PhCN})(\mu\text{-F})$ units, containing octahedrally coordinated titanium centers surrounded by three terminal fluorine atoms on the face of the octahedron and the bridging fluorine atoms in *cis*-positions with respect to each other. The structure of $\{\text{TiF}_4(\text{PhCN})\}_3$ represents the first example of a trimeric pseudo pentahalide MX_4L (M = Ti, Zr, X = halogen, D = ligand), a class of potentially interesting Lewis acids. The characterization of $\{\text{TiF}_4(\text{PhCN})\}_3$ by ^{19}F NMR revealed that in solution it dissociated to a mixture of $[\text{TiF}_3(\text{PhCN})_3]^+$, $\text{TiF}_4(\text{PhCN})_2$ and oligomers including $[\text{Ti}_4\text{F}_{18}]^{2-}$ and $\{\text{TiF}_4(\text{PhCN})\}_n$. The existence of oligomeric complexes containing *face*- $\{\text{TiF}_3(\text{PhCN})_{3-n}(\mu\text{-F})_n\}$ ($n = 1\text{--}3$) fragments was established by one- and two-dimensional variable temperature ^{19}F NMR. In contrast, TiF_4 has a low solubility in SO_2 , because the donor strength of SO_2 ($\text{DN} = 6.5 \pm 2.2 \text{ kcal mol}^{-1}$) is too weak to fully convert polymeric TiF_4 into soluble $\text{TiF}_4\text{--SO}_2$ donor–acceptor adducts. TiF_4 and MeCN ($\text{DN} = 14.1 \text{ kcal mol}^{-1}$) formed only the molecular complex $\text{TiF}_4(\text{MeCN})_2$, characterized by preliminary X-ray structure, IR and EI-MS. Thus mononuclear donor–acceptor complexes TiF_4L_2 can only be isolated from MeCN and stronger basic solvents.

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1. Introduction

Titanium tetrafluoride and Lewis bases L normally form 1:2 adducts TiF_4L_2 [1,2], while reactions with some weak Lewis bases afforded polymeric fluorine bridged complexes [2(a),3]. The formation of polynuclear Ti(IV) fluorine bridged complexes was established in solutions of TiF_4 in MeCN [3,4], Et_2O [5], TiF_4 in MeCN/ CH_2Cl_2 [4] and $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ [5] by means of ^{19}F NMR. The interaction of TiF_4 with Me_2O in SO_2 [6], $(\text{MeO})_3\text{PO}$ in MeCN [2(i)], $[\text{FSO}_3]^-$ in SO_2 , and $[\text{CF}_3\text{COO}]^-$ in MeOH also afforded mixtures of oligomeric and monomeric complexes. In all cases the relative concentration of the oligomeric complexes increased upon decreasing the amount of L relative to TiF_4 or decreasing the donor number (DN) of the solvent.

Possible structure models of oligomeric complexes in MeCN solution of TiF_4 were proposed based on the ^{19}F NMR data and suggested *face*- $\{\text{TiF}_3(\text{MeCN})_{3-n}(\mu\text{-F})_n\}$ ($n = 1\text{--}3$) fragments having terminal fluorine atoms as well as bridging fluorine atoms in *cis*-positions to each other [4]. To the best of our knowledge, no structurally characterized examples of 1 TiF_4 :1 L adducts have been reported to the date. In order to isolate these polymeric donor–acceptor adducts we reinvestigated the interaction of TiF_4 with SO_2 and MeCN, and also studied the reaction of TiF_4 with PhCN ($\text{DN} = 11.9 \text{ kcal mol}^{-1}$) [7–9], which is a weaker donor than MeCN ($\text{DN} = 14.1 \text{ kcal mol}^{-1}$) but stronger than SO_2 ($\text{DN} = 6.5 \pm 2.2 \text{ kcal mol}^{-1}$) [10]. TiF_4 and stronger donors, such as Et_2O , THF, Me_2SO , etc. [7] form TiF_4L_2 complexes as major product, and therefore these systems were not explored.

Solutions of TiF_4 in MeCN and mixtures MeCN/ CH_2Cl_2 , Et_2O , PhCN, THF are of interest due to the catalytic activity of TiF_4 complexes in reaction of 2-trimethylsilylmethyl-1,5-

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dienes with aldehydes [11], enantioselective addition of allylsilanes to aldehydes [12,13], and homoaldol addition of 1-ethoxy-1-(trimethylsilyloxy)cyclopropane to aldehydes [14,15]. The superior reactivity of TiF_4 with respect to other Lewis acid catalysts (e.g. TiCl_4 , SnCl_4 , Me_2AlCl) has been attributed to the high electronegativity of fluorine as well as to the cleavage of Ti–F–Ti bonds of oligomeric complexes during the catalytic cycle giving highly acidic Ti(IV) center [13].

2. Results and discussion

2.1. Interaction of TiF_4 with SO_2 , MeCN, and PhCN

Titanium tetrafluoride has a very low solubility in SO_2 , insoluble according to Ref. [16] precluding isolation of the crystalline donor–acceptor adduct from this solvent. However, the ^{19}F NMR spectrum of a SO_2 solution over solid TiF_4 was measured at r.t. and contained molecular oligomeric fluorine bridged complexes, while monomeric species such as $[\text{TiF}_3(\text{SO}_2)_3]^+$ and $\text{TiF}_4(\text{SO}_2)_2$ were not detected. Thus the donor power of SO_2 ($\text{DN} = 6.5 \pm 2.2 \text{ kcal mol}^{-1}$ [10]) is presumably too small to break all the fluorine bridges in solid TiF_4 , and only oligomeric complexes are detected in SO_2 solution. Resonances of terminal fluorines were located in the range 356–264 ppm, between the resonances assigned to $[\text{TiF}_3(\text{SO}_2)_3]^+$ (375 ppm) [10] and $[\text{Ti}_4\text{F}_{18}]^{2-}$ (264 ppm) [18], hence oligomeric complexes in solution contained *face*- $\{\text{TiF}_3(\text{SO}_2)_{3-n}(\mu\text{-F})_n\}$ ($n = 1\text{--}3$) fragments (Scheme 1) much like TiF_4 complexes in MeCN solution [4].

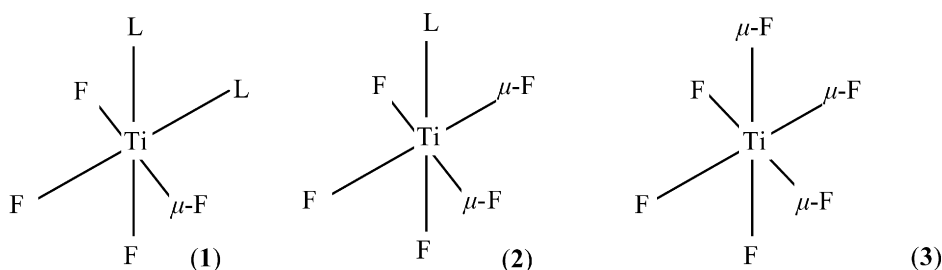
The stronger donor MeCN interacts with the TiF_4 forming oligomeric complexes as the major species in solution as well as molecular complexes $[\text{TiF}_3(\text{MeCN})_3]^+$ and $\text{TiF}_4(\text{MeCN})_2$ [3,4,17]. The solid deposited from MeCN solution was only previously characterized by elemental analysis as $\text{TiF}_4(\text{MeCN})_2$ (solid was dried under vacuum) [2(i)], while other authors [17,2(a)] reported the $\text{TiF}_4\text{-MeCN}$ adduct. In order to clarify the nature of the solid we have attempted a detailed crystallographic and spectroscopic characterization of the solid. The preliminary crystal structure is consistent with *cis*- $\text{TiF}_4(\text{MeCN})_2$, thus proving that only mononuclear complexes are obtained from MeCN solution. Two observed broad IR bands attributable to Ti–F absorption of *cis*- $\text{TiF}_4(\text{MeCN})_2$ at 675 cm^{-1} (vs), 521 cm^{-1} (vs) are characteristic for the *cis*- TiF_4L_2 adducts, e.g. *cis*- $\text{TiF}_4(\text{Me}_2\text{SO})_2$ (610 vs, 550 s) [2(b)], *cis*- $\text{TiF}_4(\text{DME})_2$ DME = dimethoxyethane (670 vs, br, 585 vs, br) [2(b)], and *cis*- $\text{TiF}_4(\text{bipy})_2$ bipy = 2,2'-bipyridyl (634 vs, br, 562 s) [2(c)]. The

addition of CH_2Cl_2 to the MeCN solution of TiF_4 increased the relative concentration of polymeric complexes in solution; however only glasses and/or oily products were obtained from these mixtures.

In order to aid crystallization MeCN was replaced by the slightly weaker donor PhCN. TiF_4 is moderately soluble in PhCN and PhCN/ CH_2Cl_2 mixtures. Solutions mainly contained oligomeric complexes and only a minor amount of *cis*- $\text{TiF}_4(\text{PhCN})_2$ (**1**) [ca. 7% total by ^{19}F NMR] (Scheme 2). For comparison the relative intensity of *cis*- $\text{TiF}_4(\text{MeCN})_2$ was 36% of total in solutions TiF_4 in MeCN at the same temperature. The relative concentration of **1** decreased by adding CH_2Cl_2 to PhCN, and the resonances of **1** were undetected for 1 TiF_4 :2 PhCN in CH_2Cl_2 (Section 3 supporting information) suggesting a lower basicity for PhCN than for the bridging fluorine toward the TiF_4 , i.e. in solution formation of fluorine bridged $\{\text{TiF}_4(\text{PhCN})\}_n$ oligomers is thermodynamically favored over *cis*- $\text{TiF}_4(\text{MeCN})_2$ in solution.

The ^{19}F NMR spectra of TiF_4 in PhCN resembles the spectrum of TiF_4 in MeCN at the same temperatures [4], suggesting a similar structure for the complexes in solution. The proposed models for MeCN adducts were given in Ref. [4]. The most downfield singlet resonance at 332.1 ppm assigned to *face*- $[\text{TiF}_3(\text{PhCN})_3]^+$, the utmost upfield resonance of terminal fluorine atoms attributed to $\text{F}_{\text{terminal}}$ atoms of $[\text{Ti}_4\text{F}_{18}]^{2-}$ [18]. We note that the singlet resonance of *face*- $[\text{TiF}_3(\text{PhCN})_3]^+$ was the strongest signal in the spectrum of TiF_4 and 1 eqv. SbF_5 in PhCN. Thus all resonance of terminal fluorine atoms are located between resonances of *face*- $[\text{TiF}_3(\text{PhCN})_3]^+$ and *face*- $\{\text{TiF}_3(\mu\text{-F})_3\}$ and belong to the *face*- $\{\text{TiF}_3(\text{PhCN})_{3-n}(\mu\text{-F})_n\}$ ($n = 1\text{--}3$) fragments of Ti(IV) oligomeric complexes (Scheme 2) similar to that for the cases discussed above with MeCN and SO_2 donors. The ^{19}F – ^{19}F COSY NMR spectra (see supporting information) showed cross-peaks between two and three $\text{F}_{\text{terminal}}$ resonances confirming the presence of species with two and three, but not more, terminal fluorine atoms.

The IR and Raman spectra of the crystalline material (shown by X-ray diffraction to be $\{\text{TiF}_4(\text{PhCN})\}_3$ (**2**), see Section 2.3) showed absorption bands attributed to the PhCN ligand [19], and Ti– $\text{F}_{\text{terminal}}$ vibrations (671 cm^{-1} (R), 681 cm^{-1} , 700 cm^{-1} (IR, R), 717 cm^{-1} (R), 728 cm^{-1} (IR), 738 cm^{-1} (R)) and Ti–($\mu\text{-F}$) vibrations (494 cm^{-1} (IR), 505 cm^{-1} (IR, R), 534 cm^{-1} (IR)). The Ti– $\text{F}_{\text{terminal}}$ and Ti–($\mu\text{-F}$) bands of **2** are comparable to those of $[\text{Ti}_4\text{F}_{18}]^{2-}$ [18]. Ti–($\mu\text{-F}$) bands of **2** are also close to those of TiF_4 [20], while Ti– $\text{F}_{\text{terminal}}$ bands of **2** are located at lower wavenumbers due to longer Ti– $\text{F}_{\text{terminal}}$ distances



Scheme 1. L = molecular donor ligand (e.g. SO_2 , PhCN, MeCN).

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