Polymer-supported Trichlorotitanium(III) Complexes and Their Dioxygen Adducts*

Yasuo Chimura, Masazo Beppu, Satohiro Yoshida, and Kimio Tarama

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

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Various polymer-supported trichlorotitanium(III) ($TiCl_3$) complexes were prepared in pyridine or THF from $TiCl_3$ and copolymers composed of 4-vinylpyridine (10, 20, and 65 mol%), divinylbenzene (0 and 20 mol%), and styrene. The ESR technique was employed for structural studies of titanium(III) species and their dioxygen adducts contained in the supported complexes. The supported complexes contained, as titanium(III) species, mainly (>88%) mixtures of $TiCl_3(pyr)_nL_{3-n}$ ($n=1$, 2, and 3), where pyr is a pyridyl group of the supports and L is a molecule of the solvents used in preparation. The relative amounts of the species having smaller n values increased with cross-linking, with a decrease in the content of pyridyl groups, and with pretreatment with tetrachlorotitanium(IV) ($TiCl_4$). On exposure to oxygen the supported complexes gave two or three kinds of dioxygen adducts ($Ti(IV)–O_2^-$) characterized by g_1, the principal g value along the axis of O–O bond. The g_1 values of three dioxygen adducts α, β, and γ were 2.027—2.028, 2.022—2.024, and 2.017—2.018, respectively. The probable structures of α, β, and γ, when L is THF, are $[TiCl_2(pyr)_3(O_2)]Cl$, $TiCl_3(pyr)_2(O_2)$, and $TiCl_3(pyr)L(O_2)$, respectively, their precursors being the titanium(III) species having the n values of 3, 2, and 1, respectively.

Many reports have appeared on dioxygen adducts of divalent cobalt and of lower valent transition metals of the group VIII.[1] Typical examples are $Co\{C_6H_5C(O^-)=CHC(CH_3)=NCH_2-\}_2(O_2)py$, $Ir(O_2)Cl(CO)\{P(C_6H_5)_3\}_2$, $Pt(O_2)\{P(C_6H_5)_3\}_2$, and $Ni(O_2)\{CNC(CH_3)_3\}_2$.

Dioxygen adducts of other metals are scarcely known. The main reason is that they react rapidly in solution with their original complexes (step b in the following scheme), even though they were once formed.

$$M + O_2 \underset{a}{\rightleftarrows} M–O_2 \xrightarrow[b]{+M} \cdots \longrightarrow M–O–M \text{ or } M=O$$

Two devices have been developed to suppress step b: (1) dioxygen adducts are sterically protected by ligands with bulky substituents from reacting with their orginal complexes;[2] (2) metal complexes are attached to organic or inorganic polymers with coordinating groups so that no two metal complexes can approach each other. Misono *et al.*[3] reported that several cobalt(II) Shiff base complexes attached to poly-4-vinylpyridine gave 1: 1 dioxygen adducts. Wang[4] reported the spectral evidence that oxygen was bound reversibly to the diethyl ester of heme embedded in a matrix of polystyrene and 1-phenethylimidazole. Leal *et al.*[5] showed recently that an iron(II) porphyrin attached to a modified silica gel adsorbed oxygen reversibly and was not oxidized to a μ-oxo dimer even at room temperature.

The ESR signals observed during the course of reaction of $TiCl_3$ with hydrogen peroxide in a flow system were ascribed to peroxy radical species of titanium.[6] No dioxygen adduct of titanium formed from a titanium(III) complex and molecular oxygen, however, has been observed in solution. We could detect a dioxygen adduct of $TiCl_3$, by binding $TiCl_3$ to a copolymer containing pyridyl groups and exposing it to oxygen.[7] The aim of the present work is to clarify the structures of titanium(III) species and of their dioxygen adducts contained in the supported $TiCl_3$ complexes.

Experimental

Materials. All solvents were refluxed over sodium metal or calcium hydride, then distilled, and stored under nitrogen. Monomers 4-vinylpyridine, styrene, and divinylbenzene were distilled under reduced pressure immediately before use. The divinylbenzene contained about 45% ethylvinylbenzene and was employed when cross-linked polymers were desired. Trichlorotitanium(III) was used as a 0.1 M acetonitrile solution. Commercial oxygen and nitrogen gases were used without further purification.

Polymer Supports: The monomers (total 50 mmol) were copolymerized by the use of 2,2′-azobisisobutyronitrile (0.25 mmole) in benzene or ethanol (50 cm^3) under nitrogen at refluxing temperature for 5 h. The resulting polymers were either precipitated by addition of ethyl ether when they were linear and soluble or washed with benzene and methanol when cross-linked and insoluble. They were then dried *in vacuo* at 120°C and ground to powders of 100—300 mesh. The yields were 60—80%. The degree of cross-linking was assumed to be equal to the molar ratio of charged divinylbenzene to total monomers. The content of pyridyl groups (mol%) was calculated from nitrogen microanalysis.

Polymer-supported $TiCl_3$ Complexes: The acetonitrile solutions of $TiCl_3$ (0.072—0.146 mmol) were stirred with the polymer supports (0.180 g, 0.145—1.15 mequiv. N) dissolved or swelled in pyridine or THF (30 cm^3) under nitrogen at room temperature for 5 h. The solvents were then evaporated *in vacuo* when the supported complexes were prepared from cross-linked supports in pyridine or from soluble, linear ones in either of the solvents, while the solvent was decanted when prepared from cross-linked ones in THF. The resulting solids were then dried *in vacuo* at room temperature. The amounts of charged $TiCl_3$ were controlled to yield supported complexes containing about 5% of $TiCl_3$ based on the total aromatic rings of the supports. Thus, in order to prepare supported complexes with 20% cross-linking and 10, 20, and 65% pyridyl group in THF, 0.146, 0.100, and 0.080 mmol of $TiCl_3$, respectively, were charged. The amounts of $TiCl_3$ corresponding to 5% of the total aromatic rings of the supports were introduced when supported complexes were prepared in pyridine.

A support with 20% cross-linking and 65% pyridyl group (0.180 g, 1.02 mequiv. N) was stirred with $TiCl_4$ (0.29 mmol) in THF (30 cm^3) for 5 h, subsequently mixed with $TiCl_3$ (0.10 mmol) and worked up as described above.

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Analysis of Titanium. The amounts of attached $TiCl_3$ were determined only in the case of supported complexes with cross-linking prepared in THF. The method was to titrate chelatometrically titanium ions not attached and dissolved in a supernatant liquid, and to subtract the titre from the amount of charged $TiCl_3$. A titanium(IV) ion is so apt to be hydrolyzed in water that a 50% aqueous ethanol solvent was employed, and EDTA added in excess was back-titrated at pH 5.5 with a 0.05 M zinc(II) solution by the use of xylenol orange as an indicator.

ESR Measurements. Fine solids of the supported complexes were transferred under nitrogen to ESR sample tubes equipped with three-way stopcocks. Their spectra were recorded under nitrogen at room temperature and 77 K with a JEOL-JES-3BS-X (X-band) spectrometer before and after contact with oxygen. The g values were calculated on the basis of that of manganese(II) ions doped into magnesium oxide, which was calibrated with an aqueous solution of peroxylamine disulfonate. The relative amounts of paramagnetic species were determined by the integration of their ESR spectra with a JEOL-JES-ID-2 integrator.

Results and Discussion

Polymer-supported $TiCl_3$ Complexes. The colors of polymer-supported $TiCl_3$ complexes depend upon the composition of supports and the solvents used in preparation (Table 1). Supported complexes without cross-linking are dark brown regardless of solvent. Those with 20% cross-linking change their colors from brown to light brown and from brown to light yellow with a decrease in the content of pyridyl groups, when they are prepared in pyridine and THF, respectively.

All the supported complexes gave two types (A and B) of ESR signals of titanium(III). Type A with g value of 1.96** was easily detected at room temperature and 77 K. Type B was very weak and broad at room temperature. On cooling down to 77 K it became strong showing g values of 1.87—1.91, but was much broader than type A. ESR spectra of a supported complex with 20% cross-linking and 65% pyridyl group prepared in pyridine recorded at room temperature and 77 K are shown in Fig. 1 as a typical example. Supported complexes without cross-linking showed, in addition to A and B signals, weak signals at $g\approx 4$ attributable to $\Delta M=\pm 2$ transitions of the triplet-state of a $TiCl_3$ dimer.[8,9]

The g values and relative amounts of the two types of signals are summarized in Table 1. Type A signals have almost constant g values throughout all the supported complexes. Their amounts are much smaller than those of type B signals, diminishing with cross-linking, a decrease in the content of pyridyl groups, the change of solvents from pyridine to THF, and pretreatment with $TiCl_4$. The g values of type B signals are greatly influenced by the solvents used in preparation, the composition of the supports, and pretreatment with $TiCl_4$. Supported complexes prepared in pyridine have larger g values than those prepared in THF except for those without cross-linking. Among supported complexes prepared in THF the g values decrease with a decrease in the content of pyridyl groups, while supported complexes prepared in pyridine have constant g values. Cross-linking makes the g value small when prepared in THF, while cross-linking has little effect when prepared in pyridine. Tetrachlorotitanium(IV) introduced prior to addition of $TiCl_3$ makes a small g value.

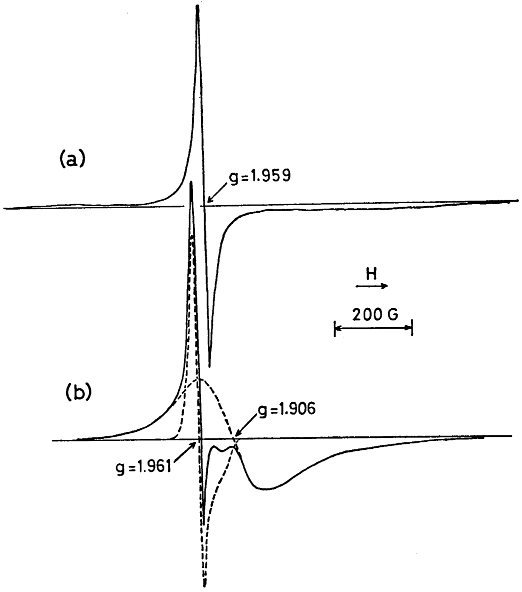


Fig. 1. ESR spectra of a supported $TiCl_3$ complex with 20% cross-linking and 65% pyridyl group prepared in pyridine, recorded under nitrogen at room temperature (a) and at 77 K (b).

When $TiCl_3$ is dissolved into pyridine, a sharp intense singlet signal at $g=1.96$[8] or 1.957[9] has been observed at room temperature along with a triplet-state spectrum of a $TiCl_3$ dimer. This signal has been ascribed to a $TiCl_3$ monomer whose structure, however, is unknown. The titanium(III) species giving type A signals has an analogous structure because of the similarity of g values and line widths between type A signals and the above signal in the pyridine solution. The titanium(III) species responsible for type A signals is coordinated only by the pyridyl groups of supports, since the g values of the signals depend neither upon the solvents used in preparation nor the composition of supports, the amounts of the signals decreasing with a decrease in chelating nature of the pyridyl groups.

Trichlorotitanium(III) forms hexacoordinated complexes of the type $TiCl_3L_3$, where L is a polar molecule such as acetonitrile, pyridine, acetone, or THF.[10] Further, $TiCl_3$ forms also hexacoordinated complexes of the type $TiCl_3L_2L'$ with two different non-halide ligands, where L and L′ are acetonitrile, dioxane, THF, and 2-propanol.[11] Thus the following hexacoordinated titanium(III) species seem to be present in the supported complexes: $TiCl_3(pyr)_nL_{3-n}$ ($n=1$, 2, and 3), where pyr is a pyridyl group of the supports and L is a molecule of the solvents used in preparation.

In frozen solution at 77 K, $TiCl_3L_3$, where L is acetonitrile, pyridine, or THF, gave an ESR signal with $g_{//}=1.883$, $g_{\perp}=1.921$, $g_{av}=1.908$;[11] $g_1=1.86$, $g_2=$

** Each g value of the two types of signals was calculated at the center of each ESR signal, since the signal was a single line without peaks giving principal g values.

TABLE 1. *g* VALUES, RELATIVE AMOUNTS OF TWO TYPES OF SIGNALS, AND COLORS OF POLYMER-SUPPORTED $TiCl_3$ COMPLEXES

Expt. No.	Solvent used for preparation	Cross-linking %	Content of pyridyl groups %	*g* Value[a] type A	*g* Value[a] type B	Relative amount[a,b] type A/type B %	Color
1	pyridine	0	65	1.962	1.909	14	dark brown
2	pyridine	20	65	1.961	1.906	2	brown
3	pyridine	20	10	1.961	1.906	1	light brown
4	THF	0	65	1.959	1.908	10	dark brown
5	THF	20	65	1.960	1.901	2	brown
6	THF	20	20	1.959	1.883	1	light brown
7	THF	20	10	1.959	1.870	1>	light yellow
8[c]	THF	20	65	1.960	1.873	1>	yellow

a) Measured under nitrogen at 77 K. b) Ratio of the areas under both types of integrated signals. c) Pretreated with $TiCl_4$.

1.89, $g_3=1.95$, $g_{av}=1.90$;[8] or $g_{//}=1.849$, $g_{\perp}=1.894$, $g_{av}=1.879$,[11] respectively, while it gave a very broad signal at room temperature.[12] Since the *g* values and the line widths of type B signals at room temperature and 77 K are similar to those of the above $TiCl_3L_3$ complexes, type B signals are ascribed to the $TiCl_3(pyr)_nL_{3-n}$ species.

In hexacoordinated titanium(III) complexes their *g* values increase with the increasing number of their ligands at higher order in the spectrochemical series.[11,13] The *g* values of the above $TiCl_3L_3$ complexes increase with the following order of L: THF<pyridine<acetonitrile. This is the same order of L in the spectrochemical series.[14]

The fact that supported complexes prepared in pyridine have larger *g* values than those prepared in THF indicates the presence of the $TiCl_3$ species having solvent molecules, *i.e.*, $TiCl_3(pyr)_nL_{3-n}$ ($n=1$ and 2), in the supported complexes. The decrease in the *g* values of supported complexes prepared in THF with a decrease in the content of pyridyl groups indicates the increase in the number of the $TiCl_3$ species having more solvent ligands, THF, with a decrease in the content of pyridyl groups. The decrease in the *g* values with cross-linking of the supports or with pretreatment with $TiCl_4$ indicates also the increase in the $TiCl_3$ species which have more solvent ligands, THF, with these changes in the conditions of preparation. Supported complexes prepared in pyridine would contain the $TiCl_3(pyr)_nL_{3-n}$ species having various values of *n*, as those prepared in THF contain, in spite of the small change of the *g* values with the change of the composition of the supports. The small change is ascribed to the similar effects of a pyridyl group (4-alkylpyridine) and pyridine upon the *g* value of a titanium(III) ion.

In conclusion, there are several $TiCl_3$ species with different environments (titanium(III) species responsible for type A signals and $TiCl_3(pyr)_nL_{3-n}$ ($n=1$, 2, and 3)) in polymer-supported $TiCl_3$ complexes, and the relative amounts of these titanium(III) species depend upon the composition of the polymer-supports (the content of pyridyl groups and the degree of cross-linking) and upon pretreatment with $TiCl_4$. In supported complexes with a high content of pyridyl groups, the pyridyl groups coordinate as chelate ligands to $TiCl_3$, and the number of the $TiCl_3$ species with two or three chelate pyridyl groups, *i.e.*, $TiCl_3(pyr)_nL_{3-n}$ ($n=2$ and 3), is large. On the other hand, such chelation is difficult in supported complexes with a low content of pyridyl groups and thus the $TiCl_3$ species with one pyridyl group, *i.e.*, $TiCl_3(pyr)L_2$, increase. Cross-linking makes supports rigid and their chelating nature weak. On addition of $TiCl_4$, the pyridyl groups coordinate as chelate ligands to $TiCl_4$ forming $TiCl_4(pyr)_2$, and thus the number of the pyridyl groups which can coordinate as chelates decreases and $TiCl_3$ added subsequently forms mainly $TiCl_3(pyr)L_2$.

Dioxygen Adducts of Polymer-supported $TiCl_3$ Complexes. By introduction of 1 atm of oxygen upon polymer-supported $TiCl_3$ complexes at room temperature, the intensities of both types of ESR signals became less than half of their original ones within a few minutes except for supported complexes without cross-linking. The colors of the supported complexes turned from brown or yellow to orange or yellowish orange at the same time. The decrease in intensities of both types of ESR signals and the change of color were very slow (half-life, *ca.* 2 h) in the case of supported complexes without cross-linking. This difference may be mainly caused by the difference in surface areas. Supported complexes with cross-linking are fine powders and may have greater surface areas than those without cross-linking which are fine pieces of films.

New sharp signals appeared at about $g=2.01$ as soon as the signals of titanium(III) diminished. The shapes of the new signals at 77 K were the same as those at room temperature. The new signals of two different supported complexes are given in Fig. 2. Each spectrum consists of two or three signals, each having three principal *g* values, *viz.*, $g_1=2.028$, $g_1'=2.023$, $g_2=g_2'=2.011$, $g_3=g_3'=2.004$ (Fig. 2a); $g_1=2.028$, $g_1'=2.022$, $g_1''=2.017$, $g_2=g_2'=g_2''=2.011$, $g_3=g_3'=g_3''=2.004$ (Fig. 2b). The new signals of all the supported complexes we examined had the following principal *g* values: $g_1=2.017$—2.028, $g_2=2.010$—2.011, and $g_3=2.003$—2.004 (Table 2). These values are nearly the same as those of O_2^- radicals on titanium dioxide.[15] Thus the new signals are ascribed to dioxygen adducts of support-

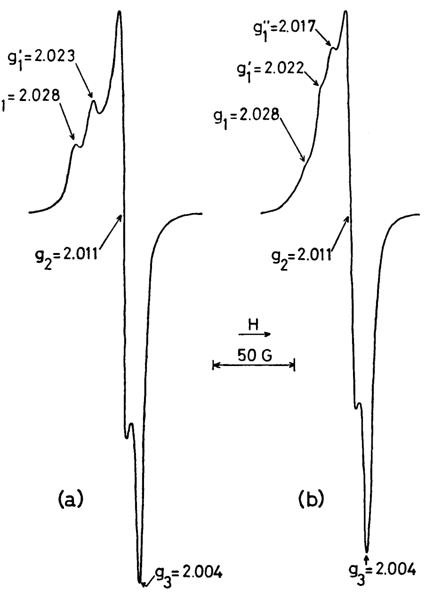


Fig. 2. New ESR signals of supported $TiCl_3$ complexes with 20% cross-linking and 65% (a) and 10% (b) pyridyl group prepared in THF, recorded under nitrogen at room temperature after contact with oxygen.

ed $TiCl_3$ complexes, whose electronic structure should be formally decribed as $Ti(IV)-O_2^-$.

The three principal g values of the dioxygen adducts of the supported complexes prepared from different supports in different solvents are given in Table 2. We denote principal g value along the axis of O–O bond by g_1. The g_1 values are greatly influenced by the conditions of preparation, whereas the g_2 and g_3 values remain nearly constant. The g_1 values can be classified into three groups: 2.027—2.028, 2.022—2.024, and 2.017—2.018. They correspond to three different $Ti(IV)-O_2^-$ species α, β, and γ, respectively, whose g_2 values as well as g_3 values are identical with each other. The g_1 peak of α is enhanced in supported complexes with a high content of pyridyl groups prepared in either of the solvents, becoming a shoulder in those with a low content of pyridyl groups. The g_1 peak of β behaves like that of α, but remains as a stronger peak than that of α when supported complexes are prepared from supports with a low content of pyridyl groups. The g_1 peak of γ appears only in supported complexes with a low content of pyridyl groups prepared in THF or pretreated with $TiCl_4$, being the strongest of the three peaks.

A few different O_2^- species have also been found on the surface of titanium dioxide. Naccache *et al.*[16] reported that two different O_2^- species were found on both anatase and rutile: $g_1=2.024$, $g_1'=2.020$, $g_2=g_2'=2.009$, $g_3=g_3'=2.003$ for anatase; $g_1=2.030$, $g_2=2.008$, $g_3=2.004$, $g_1'=2.020$, $g_2'=2.009$, $g_3'=2.003$ for rutile. Davydov *et al.*[17] found five different O_2^- species on anatase: $g_1^1=2.0330$, $g_1^2=2.0278$, $g_1^3=2.0254$, $g_1^4=2.0233$, and $g_1^5=2.0213$, the g_2 values as well as the g_3 values of which coincided with each other. However, the structures of the dioxygen adducts corresponding to these different g_1 values have not been described.

The structures of the dioxygen adducts α, β, and γ should be considered. These dioxygen adducts do not come mainly from the titanium(III) species responsible for type A signals, since the amounts of type A signals were small. There was no remarkable difference in the relative amounts of these dioxygen adducts of a supported complex with 0% cross-linking and 65% pyridyl group and that with 20% cross-linking and 65% pyridyl group, where the relative amounts of type A signals to type B signals were 14% and 2%, respectively. Adducts α and β were observed in supported complexes prepared in pyridine. They have no THF ligand though they appeared also in supported complexes prepared in THF. The relative amounts of the titanium(III) species $TiCl_3(pyr)_3$, $TiCl_3(pyr)_2L$, and $TiCl_3(pyr)L_2$ in supported complexes prepared in THF increased in this order with a decrease in the content of pyridyl groups. The relative amounts of α, β, and γ increased also in this order with a decrease in the content of pyridyl groups. Thus $TiCl_3(pyr)_3$, $TiCl_3(pyr)_2L$, and $TiCl_3(pyr)L_2$ might be the precursors of α, β, and γ, respectively.

The order of the g_1 values of α, β, and γ gives information on the structures of the dioxygen adducts. It has been shown both experimentally and theoretically that the g_1 value of a O_2^- radical coordinating to a cation approaches g_e (2.0023) more closely as the charge of the cation becomes more positive.[15] The g_1 values decreased in the order $\alpha>\beta>\gamma$, the negativity of titanium ions of the dioxygen adducts decreasing in the same order. Since a pyridyl group is more basic than THF or a chloride anion, a titanium ion which has more pyridyl

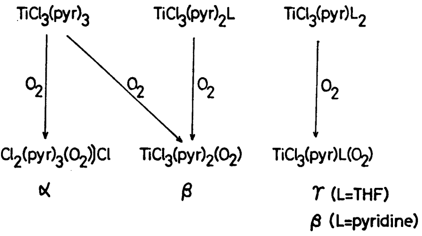
Table 2. Principal g values of dioxygen adducts of polymer-supported $TiCl_3$ complexes[a]

Expt. No.	Solvent used for preparation	Cross-linking %	Content of pyridyl groups %	g_1	g_1'	g_1''	g_2	g_3
1	pyridine	0	65	2.028	2.022	—	2.010	2.004
2	pyridine	20	65	2.028	2.023	—	2.010	2.003
3	pyridine	20	10	2.028 sh[b]	2.022	—	2.011	2.004
4	THF	0	65	2.028	2.024	—	2.010	2.004
5	THF	20	65	2.028	2.023	—	2.011	2.004
6	THF	20	20	2.027 sh	2.022 sh	2.017	2.010	2.004
7	THF	20	10	2.028 sh	2.022 sh	2.017	2.011	2.004
8[c]	THF	20	65	2.028 sh	2.022 sh	2.018	2.010	2.004

a) Measured under nitrogen at room temperature after contact with oxygen. b) Abbreviation: sh, shoulder. c) Pretreated with $TiCl_4$.

groups becomes more negative. Thus the number of pyridyl groups coordinating to the titanium ions of the dioxygen adducts increases in the order $\gamma<\beta<\alpha$.

The tentative structures of α, β, and γ which agree with the above conclusions are shown in the following scheme along with their precursors. It is assumed that an oxygen molecule behaves as a unidentate ligand and a titanium ion is hexacoordinated.



Scheme.

These dioxygen adducts were very stable at 77 K, but decomposed slowly at room temperature under either nitrogen or oxygen. Among the dioxygen adducts γ was the most unstable, half-life of which was about 1 h under oxygen at room temperature.

The total yields of the dioxygen adducts after a five minute contact with 1 atm of oxygen at room temperature were measured at 77 K under nitrogen and found to be a few percent based on the titanium(III) species reacted with oxygen.

The oxygenation of supported $TiCl_3$ complexes was almost irreversible, since the decomposition of their dioxygen adducts was very slow in a vacuum or under nitrogen as compared with their rapid formation. The decomposition would imply not only the liberation of oxygen to yield the original titanium(III) species but also irreversible oxidation to titanium(IV) species.

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