

Magnetic properties as a criterion for characterizing the thermal decomposition products and reaction pathways of trichlorotitanium(III) complexes

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Summary

Magnetic susceptibility measurements were used to characterize the thermal decomposition products of trichlorotitanium(III) complexes, $TiCl_3L_n$, $TiCl_3L_2L'$, and $TiCl_3LL_2'$, studied in the 20–400°C range. The pathways of thermal decomposition are discussed.

Introduction

In our previous papers we described the synthesis and properties of trichlorotitanium(III) complexes of general formula $TiCl_3L_n$ ($n = 3$ or 4), where $L =$ tetrahydrofuran (THF)⁽¹⁾, 1,4-dioxane⁽²⁾, aliphatic alcohols (ROH)⁽³⁾, nitriles (RCN)⁽⁴⁾, pyridine (py) and its derivatives⁽⁵⁾. Using their chemical properties (thermal decomposition and ability to participate in addition reactions), the mixed molecular ligand coordination compounds $TiCl_3L_2L'$ (1), $TiCl_3LL_2'$ (2), where $L =$ THF (1, 2), MeCN (2), $L' =$ MeCN (1), THF (2), py (1, 2), alcohol $C_nH_{2n+1}OH$, $n = 1-4$, (1, 2) were subsequently prepared and characterized⁽⁶⁻⁸⁾.

From a study of the thermal properties of the compounds prepared it was found that their decomposition routes and products formed in the process are widely affected by the ligand composition of the coordination sphere which modifies the steric and electronic environment of parent substances used.

From the magnetochemical data including results reported by other authors, together with crystal structures of trichlorotitanium(III) complexes containing THF⁽⁹⁾, *i*-PrOH⁽¹⁰⁾, MeCN⁽¹¹⁾, and py⁽¹²⁾, we propose possible stereochemical configurations for $TiCl_3L_n$, $TiCl_3L_2L'$, $TiCl_3LL_2'$, and for their thermal decomposition products.

Experimental

The trichlorotitanium(III) complexes, $TiCl_3L_n$ ($n = 3$ or 4), where $L =$ THF, alcohols ($C_nH_{2n+1}OH$, $n = 1-4$), MeCN, py and its derivatives, were prepared by reacting α - $TiCl_3$ with the ligand L , in sealed two-necked ampoules under a dry N_2 atmosphere as previously described⁽¹⁻⁵⁾. The other group of trichlorotitanium(III) complexes— $TiCl_3L_2L'$ and $TiCl_3LL_2'$ —were prepared by using exact stoichiometric ratios of reactants ($TiCl_3L_2 + L'$, $TiCl_3L + 2L'$) in hexane under nitrogen⁽⁶⁻⁸⁾. The products had compositions $TiCl_3(THF)_2L'$ (1), $TiCl_3(THF)_2L_2'$ (2), and $TiCl_3(MeCN)L_2'$ (3), where $L' =$ THF (3), MeCN (1, 2), aliphatic alcohols (1, 2, 3), py (1, 2, 3). The parent complexes $TiCl_3(THF)_2$, $TiCl_3(THF)$, and $TiCl_3(MeCN)$ were prepared by thermal decomposition of $TiCl_3(THF)_3$ and $TiCl_3(MeCN)_4$ as previously described^(1,4).

The thermal decompositions of the complexes were studied in the 20–400°C range using a thermogravimetric apparatus of our construction, which allowed measurements to be carried out in a controlled atmosphere⁽⁶⁾.

The thermal decomposition products were prepared in a special glass ampoule equipped with a glass head allowing decomposition to take place in flow nitrogen or under reduced pressure⁽²⁾.

The magnetic susceptibilities were determined by the Gouy method.

Results and discussion

The products formed by the reaction of α - $TiCl_3$ with ligand L , where $L =$ THF, aliphatic alcohols, or py and its derivatives, were found to be either $TiCl_3L_4$ ^(3,4,14-17), or $TiCl_3L_3$ ^(1,3-5,15,16,18-22), $TiCl_3L_5$ ⁽¹⁴⁾ was also very rarely formed.

On the basis of the observed temperature dependence of the effective magnetic moment and the results of electron spectroscopy, a monomeric structure and distorted octahedral stereochemical arrangement of ligands was postulated. This suggestion was confirmed by an x-ray analysis of $TiCl_3(THF)_3$ ⁽⁹⁾, $TiCl_3(i$ -PrOH)₄⁽¹⁰⁾, $TiCl_3(MeCN)_4$ ⁽¹¹⁾, and $TiCl_3(py)_4$ ⁽¹²⁾.

In the $TiCl_3L_4$ and $TiCl_3L_5$ complexes the number of possible ligands exceeds the usual coordination number, 6, for titanium(III). The magnetic susceptibility measurements (Table 1), however, are insufficient for the determination of the exact ligand composition of the coordination sphere and for the location of the seventh possible ligand, ROH. Based on the magnetic measurements and the results of halogen substitution studies, Giggenbach and Brubaker⁽¹⁴⁾ concluded that $TiCl_3(MeOH)_4$ and $TiCl_3(MeOH)_5$ are ionic and that their coordination spheres may best be described by the formulae

Table 1. Effective magnetic moments for the $TiCl_3L_5$ and $TiCl_3L_4$ compounds.

Compound	$\mu_{eff}/\mu_B(T/K)$		Ref.
$TiCl_3(MeOH)_5$	1.79(297)	1.68(78)	14
$TiCl_3(MeOH)_4$	1.81(295)	1.71(107)	13
	1.79(297)	1.69(78)	14
$TiCl_3(EtOH)_4$	1.81(300)	1.61(92)	13
$TiCl_3(i$ -PrOH) ₄	1.80(293)	1.55(77)	13
	1.74(293)	1.53(95)	15
	1.74(297)	1.52(77)	16
$TiCl_3(s$ -BuOH) ₄	1.77(293)	1.55(95)	15
$TiCl_3(cyclohexOH)_4$ ^a	1.81(293)	1.58(95)	15
$TiCl_3(MeCN)_4$	1.83(293)	1.63(77)	4
	1.75(300)		17

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^aCyclohexyl alcohol.

$[\text{TiCl}_2(\text{MeOH})_4]\text{Cl}$ and $[\text{TiCl}(\text{MeOH})_5]\text{Cl}_2$. A similar arrangement, confirmed by a crystal structure determination was reported for $\text{TiCl}_3(i\text{-PrOH})_4^{(10)}$. According to the published results, the trichlorotitanium(III) complex with *i*-propanol is composed of a dichlorotetrakis(*i*-propanol)titanium(III) cation and a chloride anion, $[\text{TiCl}_2(i\text{-PrOH})_4]\text{Cl}$. The donor atoms (2Cl + 4 O) of the ligands in the complex cation are arranged in the form of a distorted octahedron around the central atom; two chlorine atoms are in the *cis* configuration and, together with oxygen atoms, form an approximately planar arrangement in TiCl_2O_2 . The determined chemical properties do not exclude the existence of a similar ionic structure also in other TiCl_3L_4 -type alcoholic complexes.

On the other hand, the $\text{TiCl}_3(\text{MeCN})_4$ complex is neutral. According to published structural data⁽¹¹⁾ the central titanium(III) atom is coordinated to three nitrogen donor atoms and three chlorine atoms, forming a distorted octahedral arrangement (local symmetry of molecule $\text{TiCl}_3(\text{MeCN})_3$ is near C_{2v}). The fourth acetonitrile molecule is uncoordinated and is present in the solvate $[\text{TiCl}_3(\text{MeCN})_3](\text{MeCN})$. The release of one molecule of acetonitrile at relatively low temperatures corroborated this structural conclusion^(4,17). A similar ligand arrangement was also found in crystals of the $[\text{TiCl}_3(\text{py})_3](\text{py})$ complex⁽¹²⁾.

The magnetic properties of the TiCl_3L_3 -type complexes, listed in Table 2, are typical of a monomeric structure and parameters obtained by the Figgis method^(1,13,23), together with diffuse reflectance spectra, show a distorted octahedral coordination of the central titanium(III) atom, as it is also evident from the published crystal data on the neutral $\text{TiCl}_3(\text{THF})_3$ complex⁽⁹⁾.

Trichlorotitanium(III) complexes containing two molecular ligands (TiCl_3L_2) were prepared by thermal decomposition of $\text{TiCl}_3(\text{THF})_3$, $\text{TiCl}_3(\text{THF})(\text{MeCN})_2$, $\text{TiCl}_3(\text{THF})_2(\text{py})$, $\text{TiCl}_3(\text{THF})(\text{py})_2$, and $\text{TiCl}_3(\text{MeCN})(\text{py})_2$ in the 100–150°C range. As observed, in the decomposition step a whole molecule of the non-halide ligands is released and theoretically two structural

Table 2. Effective magnetic moments for the TiCl_3L_3 compounds.

Compound	$\mu_{\text{eff}}/\mu_{\text{B}}(\text{T/K})$	Ref.
$\text{TiCl}_3(\text{THF})_3$	1.82(293)	1.62(77) 1
	1.83(293)	1.64(95) 15
	1.72(283)	1.59(81) 19
$\text{TiCl}_3(n\text{-PrOH})_3$	1.81(295)	1.61(80) 13
$\text{TiCl}_3(n\text{-BuOH})_3$	1.79(295)	1.61(80) 13
$\text{TiCl}_3(i\text{-BuOH})_3$	1.86(293)	1.63(77) 13
$\text{TiCl}_3(\text{MeCN})_3$	1.84(293)	1.59(77) 4
	1.71(299)	1.57(84) 18
	1.68(302)	1.55(79) 19
$\text{TiCl}_3(\text{VinCN})$	1.81(293)	1.60(77) 4
$\text{TiCl}_3(\text{py})_3$	1.76(293)	1.49(77)
	1.63(293)	20
$\text{TiCl}_3(2\text{-Mepy})_3^a$	1.83(293)	1.35(77)
$\text{TiCl}_3(3\text{-Mepy})_3^b$	1.82(293)	1.58(77)
$\text{TiCl}_3(4\text{-Mepy})_3^c$	1.84(293)	1.56(77)
	1.75(301)	1.58(83) 24

^a2-Mepy = *o*-picoline; ^b3-Mepy = *m*-picoline; ^c4-Mepy = *p*-picoline

Table 3. Effective magnetic moments for the TiCl_3L_5 and TiCl_3L compounds.

Compound	$\mu_{\text{eff}}/\mu_{\text{B}}(\text{T/K})$	Ref.
$\text{TiCl}_3(\text{THF})_2$	1.73(296)	1.65(103) 1
	1.74(290)	1.64(82) 25
$\text{TiCl}_3(\text{py})_2$	1.82(293)	1.51(77)
$\text{TiCl}_3(\text{THF})(\text{py})$	1.74(293)	1.48(77)
$\text{TiCl}_3(\text{THF})(\text{MeCN})$	1.42(293)	0.85(77) 31
	($J = -85 \text{ cm}^{-1}$)	
$\text{TiCl}_3(\text{THF})$	1.14(295)	0.46(80) 1
	($J = -185 \text{ cm}^{-1}$)	
$\text{TiCl}_3(\text{MeCN})$	1.02(297)	0.43(77) 16
	1.40(293)	0.46(77) 4
	($J = -160 \text{ cm}^{-1}$)	
$\text{TiCl}_3(\text{VinCN})$	1.37(297)	1.09(77) 16
	1.43(293)	1.22(77) 4

arrangements might arise. Consequently the substances formed in the process could be either monomeric with the titanium(III) coordination number lowered to 5, or polymeric with a six-coordination ligand arrangement.

As a criterion for recognizing this structure difference the magnetic susceptibility measurements are useful and convenient. From the anomalously low value for μ_{eff} in $\text{TiCl}_3(\text{THF})(\text{MeCN})$ (Table 3) it is evident that only in this case does the polymerization process occur. The near octahedral coordination was confirmed by the diffuse reflectance spectrum⁽⁶⁾. The exchange interaction energy, evaluated using the Ising model⁽²⁶⁾, is characteristic of antiferromagnetic superexchange interactions between the central titanium(III) atoms *via* chlorine bridges.

Over against the diffuse reflectance spectra^(1,8) together with μ_{eff} values presented in Table 3, are consistent with a monomeric structure and trigonal bipyramidal coordination of ligands in the $\text{TiCl}_3(\text{THF})_2$, $\text{TiCl}_3(\text{py})_2$, and $\text{TiCl}_3(\text{THF})(\text{py})$ complexes.

For the $\text{TiCl}_3(\text{THF})$ and $\text{TiCl}_3(\text{MeCN})$ compounds prepared by thermal decomposition of $\text{TiCl}_3(\text{THF})_3$ and $\text{TiCl}_3(\text{MeCN})_4$, respectively, at *ca.* 150°C, the magnetic properties reveal a polymeric arrangement with antiferromagnetic exchange interaction between the paramagnetic titanium(III) centres probably through chlorine bridges. The results supporting the trigonal bipyramidal ligand coordination are discussed elsewhere^(1,4). A similar conclusion can be drawn also for the acrylonitrile complex $\text{TiCl}_3(\text{VinCN})$.

In the group of alkoxide compounds, prepared by pyrolysis (at *ca.* 100–150°C) of $\text{TiCl}_3(\text{ROH})_n$, where $n = 3$ or 4, $\text{R} = \text{Me}, \text{Et}, n\text{-Pr}, i\text{-Pr}, n\text{-Bu},$ and *i*-Bu, the formation of polymeric species was confirmed from the magnetochemical viewpoint (Table 4). Considering the solved structure of the complex with *i*-propanol⁽¹⁰⁾ during the pyrolysis step joining of structural units leading to polymeric chains with the original near octahedral arrangement is believed to occur. The release of the corresponding alcohol and HCl was estimated using gas chromatography and argentometric methods. The values of exchange energy interaction J (Table 4) are typical of relatively strong intramolecular interaction between titanium(III) atoms through oxygen bridges. These findings are in good agreement with assumptions presented elsewhere^(14,28–30). Based on magnetochemical measurements for titanium(III) methoxides and ethoxides,

Table 4. Effective magnetic moments for the $\text{TiCl}_{3-x}(\text{OR})_x$ compounds^a.

Compound	$\mu_{\text{eff}}/\mu_{\text{B}}(\text{T/K})$	
$\text{TiCl}_{2.7}(\text{OMe})_{0.3}(\text{MeOH})_{2.9}$	1.57(295) ($J = -25 \text{ cm}^{-1}$)	1.43(81)
$\text{TiCl}_{1.74}(\text{OMe})_{1.26}$	0.51(291) ($J = -700 \text{ cm}^{-1}$)	0.39(138)
$\text{TiCl}_{1.86}(\text{OEt})_{1.14}$	0.50(293) ($J = -750 \text{ cm}^{-1}$)	0.27(77)
$\text{TiCl}_{1.6}(\text{n-OPr})_{1.4}$	0.64(295) ($J = -490 \text{ cm}^{-1}$)	0.34(83)
$\text{TiCl}_{1.4}(\text{i-OPr})_{1.6}$	0.63(290) ($J = -520 \text{ cm}^{-1}$)	0.48(201)
$\text{TiCl}_{1.55}(\text{n-OBu})_{1.45}$	0.59(293) ($J = -580 \text{ cm}^{-1}$)	0.51(175)
$\text{TiCl}_{1.7}(\text{i-OBu})_{1.3}$	0.59(293) ($J = -560 \text{ cm}^{-1}$)	0.32(77)

^aRef. 27**Table 5.** Effective magnetic moments for the $\text{TiCl}_3\text{L}_2\text{L}'$ compounds.

Compound	$\mu_{\text{eff}}/\mu_{\text{B}}(\text{T/K})$	Ref.
$\text{TiCl}_3(\text{THF})_2(\text{MeCN})$	1.78(293) 1.77(297)	1.64(77) 1.60(77)
$\text{TiCl}_3(\text{THF})_2(\text{py})$	1.81(293)	1.51(77)
$\text{TiCl}_3(\text{THF})_2(\text{MeOH})$	1.86(293)	1.67(77)
$\text{TiCl}_3(\text{THF})_2(\text{EtOH})$	1.82(293)	1.63(77)
$\text{TiCl}_3(\text{THF})_2(\text{i-PrOH})$	1.88(293)	1.62(77)
$\text{TiCl}_3(\text{THF})_2(\text{n-BuOH})$	1.81(293)	1.61(77)
$\text{TiCl}_3(\text{THF})_2(\text{i-BuOH})$	1.94(293)	1.62(77)

Table 6. Effective magnetic moments for the $\text{TiCl}_3\text{LL}_2'$ compounds.

Compound	$\mu_{\text{eff}}/\mu_{\text{B}}(\text{T/K})$	Ref.
$\text{TiCl}_3(\text{THF})(\text{MeCN})_2$	1.70(293)	1.43(77)
$\text{TiCl}_3(\text{THF})(\text{py})_2$	1.80(293)	1.52(77)
$\text{TiCl}_3(\text{MeCN})(\text{THF})_2$	1.79(293)	1.64(77)
$\text{TiCl}_3(\text{MeCN})(\text{py})_2$	1.75(293)	1.48(77)
$\text{TiCl}_3(\text{MeCN})(\text{MeOH})_2$	1.76(293)	7
$\text{TiCl}_3(\text{MeCN})(\text{EtOH})_2$	1.79(293)	7
$\text{TiCl}_3(\text{MeCN})(\text{n-PrOH})_2$	1.78(293)	7
$\text{TiCl}_3(\text{MeCN})(\text{n-BuOH})_2$	1.79(293)	7
$\text{TiCl}_3(\text{MeCN})(\text{i-BuOH})_2$	1.80(293)	7

synthesized directly, a polymeric arrangement of species with strong antiferromagnetic interaction approaching nearly diamagnetism was proposed.

Whereas the process of alkoxide formation seems to be irreversible, the thermal decomposition products of trichlorotitanium(III) complexes containing proton-free ligands are believed to possess a higher reactivity, e.g. in addition with further molecular ligands. Two types of substances (see Experimental) were prepared and studied. Their μ_{eff} values, listed in Tables 5 and 6, are indicative of a monomer structure. It may be concluded that, during the reaction, the change from trigonal bipyramidal to distorted octahedral coordination occurs. In the group of $\text{TiCl}_3\text{LL}_2'$ -type complexes besides the addition, depolymerization also occurs. The results of magnetic susceptibility measurements of complexes $\text{TiCl}_3(\text{THF})_2$ -

(MeCN) and $\text{TiCl}_3(\text{THF})(\text{MeCN})_2$ ^(31,16) corroborated this suggestion.

The thermal decomposition products of this group of substances (formed between 100–150°C) from the magnetochemical point of view possess either monomeric [$\text{TiCl}_3(\text{py})_2$, $\text{TiCl}_3(\text{THF})(\text{py})$] or polymeric [$\text{TiCl}_3(\text{MeCN})(\text{THF})$, $\text{TiCl}_{3-x}(\text{OR})_x(x < 3)$] structure arrangement (Tables 3 and 4).

Conclusion

From a comparison of the magnetic properties of the group of trichlorotitanium(III) complexes under investigation, and their thermal decomposition products, it is evident that the course of decomposition varies depending upon the properties of ligands present in the parent substances.

1. In the group of complexes containing aprotic ligands (ethers, nitriles) molecules of non-halide ligands were released and formation of either monomers with lowered coordination number, or polymers exhibiting antiferromagnetic exchange interaction through chlorine bridges, was observed. The ability of these thermal decomposition products to react with further molecular ligands was observed and utilized for syntheses of mixed-ligand trichlorotitanium(III) complexes with heterogeneous coordination sphere.

2. In the course of thermal decomposition of complexes containing aliphatic alcohols, partial alcoholysis occurs as a result of the release of HCl and the corresponding alcohol; polymeric products [$\text{TiCl}_{3-x}(\text{OR})_x$] containing alkoxide groups are formed.

3. This same phenomenon was also observed in the course of thermal decomposition of $\text{TiCl}_3\text{L}_2(\text{ROH})$ and $\text{TiCl}_3\text{L}(\text{ROH})_2$. The pathway of thermal decomposition of this group of complexes is determined by the influence of coordinated aliphatic alcohols.

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(Received 3 April 1991)

TMC 2507