Thermogravimetric and spectral study of some chloro(nitrile)titanium(III) complexes

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Titanium(III) chloride reacts with nitrile ligands to form the complexes TiCl₃·3RCN (R = CH₃, CH₂=CH, C₆H₅, C₆H₅CH₂), and TiCl₃·4CH₃CN. The thermal decomposition reactions of these complexes were studied by thermogravimetric method in nitrogen atmosphere and under reduced pressure. The intermediates were isolated and identified by chemical and physical methods.

Хлорид титана(Ш) взаимодействует с нитрильными лигандами с образованием комплексов TiCl₃·3RCN (R = СН₃, СН₂=СН, С₆Н₅, С₆Н₅СН₂) и TiCl₃·4CH₃CN. Реакции термического разложения этих комплексов были изучены термогравиметрическим методом в атмосфере азота и при пониженном давлении. Промежуточные продукты были изолированы и идентифицированы при помощи химических и физических методов.

Until recently relatively few data have been reported relating to the preparation and examination of chemical properties and structure of trichloro(nitrile)titanium(III) complexes largely because of the air-sensitive nature of these compounds. The best known is the adduct TiCl₃·3CH₃CN [1—4]. The diffuse reflectance and solution electronic spectra [1—6], infrared spectra [1—3, 7], e.s.r. [5, 8] and n.m.r. [9—11] data, and electrical conductance measurements [1—3] of this compound in acetonitrile solution are best accounted for by the formulation mer-[TiCl₃(CH₃CN)_3] (symmetry point group C₂v, [8]). On the basis of infrared spectra it is now accepted that coordinated acetonitrile behaves as a normal nitrogen σ-donor ligand [12, 13] with respect to coordination with titanium(III) central atom. Such monomeric distorted octahedral structure is consistent with the room-temperature magnetic moment close to the spin-only value for a d¹ ion [3]. Previous workers have reported sometimes inconsistent significantly lower magnetic data [1, 2].

In contrast, titanium(III) chloro complexes containing coordinated molecules of other nitriles, such as C₂H₅CN [2, 4], n-C₃H₇CN [14], and acrylonitrile [14, 15]

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have received extremely limited attention. Titanium(III) chloride has been shown to react with alkyl cyanides, RCN, to give TiCl$_3$·3RCN. From reaction of TiCl$_3$ and acrylonitrile, no pure compound could be isolated despite considerable variation of the reaction conditions [15].

Little work has been done with the intermediates of thermal decomposition of chloro(nitrile)titanium(III) complexes because of the experimental difficulties involved in their isolation and characterization. Green coloured [4] (according to [5] brown) product TiCl$_3$·CH$_3$CN was prepared by vacuum decomposition of TiCl$_3$·3CH$_3$CN at selected temperature.

In the previous communication from this laboratory we reported the preparation and thermal decomposition reactions of complexes TiCl$_3$·4CH$_3$CN, TiCl$_3$·3CH$_3$CN, and TiCl$_3$·CH$_3$CN in a preliminary form [16]. The adduct TiCl$_3$·4CH$_3$CN which has been assigned the formula [TiCl$_3$(CH$_3$CN)$_3$]·CH$_3$CN, decomposed to TiCl$_3$·3CH$_3$CN very rapidly upon heating and even upon standing at room temperature for several days. This is in agreement with the finding that TiCl$_3$·4CH$_3$CN can hardly be obtained pure, although its X-ray powder pattern demonstrated its presence.

The present paper reports the extension of this work to similar nitrile complexes of titanium(III) chloride. The thermogravimetric study of coordination compounds of the type TiCl$_3$·nRCN (R = CH$_3$, CH$_2$=CH, C$_6$H$_5$, C$_6$H$_5$CH$_2$; n = 1, 3, 4) is reported for the first time.

**Experimental**

Because of the extreme ease with which the titanium(III) complexes react with oxygen and moisture, special precautions were taken to avoid oxidation and hydrolysis of the compounds synthesized. All reactions and operations were carried out in an atmosphere of dry oxygen-free nitrogen or argon. Nitrogen from a high-pressure cylinder was passed through a heated activated copper column and through a column filled with reduced Phillips catalyst containing surface chromium(II) oxide deposited on silica gel [17] for removing traces of oxygen. Deoxygenated nitrogen was further dried by passing through the columns filled with molecular sieve, type 4A (trade mark Nalsit 4) as well as through freezing traps cooled with liquid nitrogen. All experiments were carried out in special all-glass equipment connected to a nitrogen manifold under an overpressure of about 1—2 kPa above atmospheric to prevent decomposition of synthesized complexes under reduced pressure. Samples were sealed under nitrogen in glass tubes.

**Reagents**

$\alpha$-Titanium(III) chloride, supplied by the Research Institute of Macromolecular Chemistry in Brno, after purification from the sorbed titanium(IV) chloride was considered free of titanium(IV).
Acetonitrile, acrylonitrile, benzonitrile, and benzyl cyanide were obtained in reagent grade purity from Fluka, A.G. Acetonitrile, stored over molecular sieve (Nalsit 4), was purified by usual method [3, 18] immediately before use. Acrylonitrile was refluxed under reduced pressure over calcium hydride and freshly distilled into transfer flask containing hexane as diluent.

Hexane and benzene used were purified by repeated distillation under nitrogen from calcium hydride with a final distillation from violet solution of benzophenone ketyl potassium.

**Compound preparation**

The methods of synthesis were similar to those we reported earlier for trichlorotris(pyridine)titanium(III) [19, 20] and trichlorotris(tetrahydrofuran)titanium(III) [21].

\[ \text{TiCl}_3 \cdot 4\text{CH}_3\text{CN} \]

About 300 g of acetonitrile was condensed into a reaction bulb containing titanium(III) chloride (65 mmol). Reaction flask was sealed under nitrogen and the resulting mixture was stirred overnight at room temperature. Blue crystals obtained in this manner were filtered under nitrogen on a medium grade sintered glass funnel, washed on a glass frit with hexane and dried under a stream of nitrogen. The analytical data correspond to those for \( \text{TiCl}_3 \cdot 4\text{CH}_3\text{CN} \) [16]. A further amount of the adduct was obtained by partial evaporation of the filtrate that had been prepared under reduced pressure at room temperature. Difficulty was experienced in obtaining analytically pure samples of this thermally very unstable substance. After a few hours, when kept under reduced pressure at room temperature, it lost one molecule of \( \text{CH}_3\text{CN} \) and was converted to blue microcrystalline \( \text{TiCl}_3 \cdot 3\text{CH}_3\text{CN} \).

\[ \text{TiCl}_3 \cdot 3\text{C}_6\text{H}_5\text{CH}_2\text{CN} \]

This compound was prepared essentially in the same way. The blue-violet crystalline product was washed with benzene and evacuated at room temperature. Often some solvent is incorporated into the product.

\[ \text{TiCl}_3 \cdot 3\text{C}_6\text{H}_5\text{CN} \]

This compound was prepared as above except that the reaction system was rotated at room temperature for a week during which time dark green solution was obtained. An equal quantity of hexane was added to the solution while the mixture was vigorously stirred. The greenish-brown crystalline solid was washed with hexane and pumped to remove any solvent.

\[ \text{TiCl}_3 \cdot 3\text{CH}_2=\text{CHCN} \]

A large excess of 1 molar solution of acrylonitrile was treated with finely divided titanium(III) chloride. Bulb containing reaction mixture was sealed under nitrogen and the content of the reaction flask was stirred for 24 h at room temperature. Filtrations and washings with hexane were all performed by the application of nitrogen under pressure and/or by suction. The microcrystalline product was dried under reduced pressure. The analytical data are in agreement with the stoichiometry of \( \text{TiCl}_3 \cdot 3\text{C}_2\text{H}_3\text{CN} \).
The adducts prepared are soluble in their own nitrile ligands and are only poorly soluble in solvents with which they do not react. The acrylonitrile and benzonitrile complexes are soluble in chloroform, benzene, and similar aromatic solvents.

**Analytical methods**

Titanium was determined with three methods that gave close agreement. Ti(III) was determined by titration with Ce(IV) sulfate. The total titanium content was determined either spectrophotometrically as the Ti(IV) hydrogen peroxide complex, or gravimetrically as TiO₂. Chloride was determined by the Volhard method. The actual mole ratios of acetonitrile and acrylonitrile to titanium(III) chloride were determined by thermogravimetric analysis. The analyses were close to the theoretical values calculated for individual adducts.

**Thermal investigation**

All synthesized compounds were investigated by thermogravimetric method in a quartz spiral thermobalance described by us previously [22]. Measurements were performed under two different experimental conditions: in dynamic atmosphere of purified nitrogen or argon (1 l h⁻¹) and under reduced pressure (10—15 Pa). The heating rate was 4°C min⁻¹. The sample masses ranged from 20 to 50 mg.

The intermediates and the products of thermal decomposition have been isolated and characterized. In order to isolate them, the starting complexes were heated under stirring in special glass tube under experimental conditions similar to those applied in thermogravimetric experiments at temperatures corresponding to the individual steps of thermal decomposition, according to the respective thermoanalytical curves. The preparative procedure was described earlier [23]. The synthesized intermediates and products were checked by thermogravimetric and chemical analysis.

**Physical measurements**

Infrared spectra were obtained from mulls in mineral oil and hexachlorobutadiene using a Perkin—Elmer 221 spectrophotometer between NaCl plates. Sampling procedure and equipment for filling alkali halide plates in inert atmosphere and without the use of glove box were described by us in paper [24].

The diffuse reflectance spectra were determined with a VEB Zeiss Spekol spectrophotometer furnished with the reflectance attachment Model RD/0 using special all-glass cell for obtaining spectra of the air-sensitive samples. The samples used for the measurements in visible region were not diluted. The spectra were measured with respect to a magnesium oxide standard. The intensities were expressed in terms of the Kubelka—Munk function.

A special device (Fig. 1) was used for charging the reflectance spectroscopy cells under inert atmosphere. The device was first purged with purified nitrogen introduced through the valve 1 and through a capillary tube inserted into the opening 2. While nitrogen was kept
Fig. 1. A device for charging the reflectance spectroscopy cells in an inert atmosphere.

streaming in through the valve 1, the cell 3 was charged with the specimen from the originally sealed tube 6 through the opening 2. Then the cell was closed with the lid 4, which, on its inner side, was lined with a thin layer of Canada balsam. After closing the cell the underpressure in the tube 7, which was mounted with a perforated rubber cup holding the lid in its place, was released with the aid of the valve 8. The charged and closed cell was then removed from the device with the aid of the holder 5.

Magnetic susceptibility was measured by the Gouy method as it is described in [26]. Samples were sealed from the air.

The X-ray powder measurements were taken with the Philips 1540 diffractometer using CuKα radiation and Ni filter. Experimental technique for preparation of flat powdered samples of air-sensitive substances for X-ray measurements in an inert atmosphere without the application of glove box was described in the previous communication [25].

Results and discussion

No detailed thermogravimetric studies of the chloro(nitrile)titanium(III) complexes have been reported, although a brief mention of the thermal decomposition of TiCl₃·3CH₃CN has appeared in two previous publications [4, 5].

The thermal decomposition of coordination compounds containing nitrile ligands begins with the release of the coordinated nitrile, i.e. by breaking of the bonding central atom—nitrogen donor atom of the nitrile molecule. Therefore, an investi-
igation of the thermal decomposition of this type may supply information on the factors influencing the strength of this bond. Since the decomposition temperature largely depends on the physical properties (i.e. dispersity) of the investigated sample, on the experimental conditions, and on the sensitivity of the thermoanalytical instrument, it may be concluded that the thermal stability temperature cannot be absolutely assigned to the start of thermal decomposition [37—39]. Comparative data could be obtained only by determining the thermal behaviour of a whole series of compounds under identical conditions.

Examination of the thermogravimetric curve of TiCl$_3$·4CH$_3$CN (Fig. 2) indicates three steps in which the decomposition under nitrogen atmosphere proceeds. The mass loss over the temperature range 70—100°C is 13%, which agrees very well with expected value (13%) for the release of one molecule of uncoordinated acetonitrile from the crystal structure. In the temperature range 120—150°C a further 27% mass loss occurs corresponding fairly well to the loss of additional two molecules of coordinated acetonitrile. The third step commences at ca. 200°C, proceeds slowly until 240°C, when the reaction becomes more rapid leading to a final mass loss of 53%. This value is a little higher than predicted for the formation of titanium(III) chloride. In order to confirm that the titanium(III) chloride was the final product, the residue was subjected to X-ray analysis and its chemical composition was determined. The powder diffraction pattern indicates the final product of thermal decomposition of TiCl$_3$·4CH$_3$CN in nitrogen atmosphere to be crystalline γ-TiCl$_3$ (ASTM 18-1396).

The course of the thermal decomposition of TiCl$_3$·4CH$_3$CN under reduced pressure (Fig. 2) differs markedly from that in nitrogen atmosphere. The thermogravimetric curve shows the first mass loss in the temperature range 60—110°C indicating that in the first step three acetonitrile molecules are liberated simultaneously. Above 110°C a further progressive loss of mass is observed which finally
at about 260°C reaches a value of 60%. This value is much higher than that predicted for the formation of TiCl$_3$ (51.5%). The final mass loss is connected with the disproportionation of titanium(III) chloride leading to the residue the mass of which corresponds exactly to that of titanium(II) chloride (18.7%). It is important to point out that the properties of the black residue of TiCl$_2$ depend on the reaction conditions under which it has been formed. When the thermal decomposition was done under reduced pressure with trace concentration of argon atmosphere, the pyrolysis residue is pyrophoric and its X-ray diffraction pattern indicates the presence of TiCl$_2$. On the other hand, when traces of nitrogen were present in the atmosphere in the course of disproportionation under reduced pressure, the black final solid product was contaminated by titanium nitride.

On comparing the course of the thermal decomposition of TiCl$_3$·4CH$_3$CN with that of the corresponding triadduct, it may be seen that there is a good agreement between the results of both of these experiments. The actual and theoretical mass losses agree fairly well for TiCl$_3$·3CH$_3$CN (Fig. 3). The first stage, shown by the thermogravimetric curve, occurs in the range 50—120°C. The mass loss of 33% is only a little higher than that expected for the loss of two molecules of acetonitrile (29.6%). The second stage begins at ca. 170°C and proceeds slowly until 200°C to a total mass loss of 52%. This value is much higher than that expected for the loss of all three molecules of coordinated acetonitrile (44.4%). After removing the furnace titanium(III) chloride was found to be present in the cooler parts of the tube, indicating that a part of the sample was volatilized during decomposition.

On heating the sample of TiCl$_3$·3CH$_3$CN under reduced pressure in the tube of thermogravimetric balance, a progressive mass loss takes place at temperatures above 50°C which reaches a final value of 81% at about 350°C (Fig. 3). Because of high dispersity of the initial compound, prepared by thermal decomposition of TiCl$_3$·4CH$_3$CN, it is impossible to distinguish the stepwise loss of individual ligands

![Fig. 3. Thermogravimetric curves of TiCl$_3$·3CH$_3$CN in nitrogen atmosphere (—) and under reduced pressure (— — —).](image-url)
on the thermogravimetric curve. Hence, it may be concluded from this experiment, that the thermal decomposition of titanium(III) nitrile complexes under reduced pressure is not a convenient procedure for preparation of intermediate products.

The trichlorotris(acrylonitrile)titanium(III) exists in the powder crystalline form (Fig. 6). The process of its thermal decomposition involves, as a first step, the removal of two molecules of acrylonitrile from the coordination sphere (Fig. 4). During this process, the solid intermediate is partially dissolved in the excess of liberated ligand. The second mass loss corresponds to the splitting off and evaporation of the third molecule of acrylonitrile and leads to the formation of brownish-violet pyrophoric X-ray amorphous titanium(III) chloride. The actual and theoretical mass losses (36 and 55% vs. 33.8 and 50.7%, respectively) agree fairly well with the composition of TiCl$_3$·3C$_2$H$_3$CN.

In the case of TiCl$_3$·3benzonitrile and TiCl$_3$·3benzyl cyanide, the course of their thermal decomposition (Fig. 5) is generally analogous to that of TiCl$_3$·3acrylo-
When heated under reduced pressure, their thermal decomposition of both complexes was found to proceed essentially in one step only. The final products represented by a lower plateau on the decomposition curves correspond to the titanium(II) chloride formed by disproportionation of the parent complexes.

For a better understanding of the thermal stability of the complexes and of their thermal decomposition process, some of intermediate decomposition products were prepared under conditions similar to those applied in thermal investigation. The probable structure of starting compounds and intermediates has been interpreted on the basis of their visible diffusion reflectance spectra, infrared spectra, and magnetic susceptibility data.

We have already briefly commented [16] on the preparation and thermal analysis of TiCl$_3$·4CH$_3$CN. On the basis of the X-ray diffraction patterns, diffuse reflectance spectra, infrared spectra, and magnetic measurements we have concluded that this compound is different in crystal structure from TiCl$_3$·3CH$_3$CN. From our finding follows that the fourth molecule of acetonitrile is not sorbed, but it is present uncoordinated between the octahedra [TiCl$_3$(CH$_3$CN)$_3$] in the crystal structure of the solvate [TiCl$_3$(CH$_3$CN)$_3$]·CH$_3$CN first of all for crystal packing purposes.

From the comparison of the diffuse reflectance spectra of TiCl$_3$·CH$_3$CN, TiCl$_3$·3CH$_3$CN (Fig. 7), and TiCl$_3$·3C$_2$H$_5$·CHCN (Fig. 8) it could be concluded that similar coordination exists in these trichloro(nitrile)titanium(III) complexes. The absorption bands in the diffuse reflectance spectra of the above-mentioned compounds, found at 17 200 and 14 700 cm$^{-1}$ (in excellent agreement with previous results for TiCl$_3$·3CH$_3$CN [1, 2, 5]) can be assigned to the transitions of $^2B_2 \rightarrow ^2B_1$ and $^2B_2 \rightarrow ^2A_1$ characteristic of the distorted octahedral coordination of Ti(III) atom.

On the other hand, there is little agreement between the results of magnetic measurements reported here and those reported previously by various authors [1—5]. Similar discrepancies could be cited for colour of the intermediate TiCl$_3$·CH$_3$CN [4, 5]. These differences are probably due to the unequal purity of the samples investigated.

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The almost identical values of the magnetic moments (1.81—1.84 B.M.) obtained by us (Table 1) are in agreement with the monomeric structure and distorted octahedral coordination of the above-mentioned three trichlorotris(nitrile)titanium(III) complexes. On the contrary, the strongly depressed values (1.40 and 1.43 B.M.) (Table 1) of the magnetic moments of the intermediate compounds TiCl$_3$·CH$_3$CN and TiCl$_3$·CH$_2$·CHCN indicate the existence of magnetic interactions between the titanium(III) atoms via chloride bridges. Thus, it seems likely, that these compounds are coordination polymers with a structure most probably similar to that of TiCl$_3$·C$_4$H$_8$O [34].
Table 1

Magnetic moments and infrared spectral data of trichlorotris(nitrile)titanium(III) complexes in the solid state

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>$\mu_{\text{eff}}$ (293 K) B.M.</th>
<th>$\nu$(C≡N) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl$_3$·4CH$_3$CN</td>
<td>blue</td>
<td>1.83</td>
<td>2300, 2260</td>
</tr>
<tr>
<td>TiCl$_3$·3CH$_3$CN</td>
<td>blue</td>
<td>1.84</td>
<td>2300</td>
</tr>
<tr>
<td></td>
<td>blue</td>
<td>1.58—1.68 [1]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>blue</td>
<td>1.58 [2]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>blue</td>
<td>1.71 [3]</td>
<td></td>
</tr>
<tr>
<td>TiCl$_3$·CH$_3$CN</td>
<td>green</td>
<td>1.40</td>
<td>2325</td>
</tr>
<tr>
<td></td>
<td>green</td>
<td>1.37 [4]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>brown</td>
<td>1.37 [5]</td>
<td></td>
</tr>
<tr>
<td>TiCl$_3$·3CH$_2$:CHCN</td>
<td>brownish-green</td>
<td>1.81</td>
<td>2275</td>
</tr>
<tr>
<td>TiCl$_3$·CH$_2$:CHCN</td>
<td>brown</td>
<td>1.43</td>
<td>2245</td>
</tr>
<tr>
<td>TiCl$_3$·3C$_6$H$_5$CN</td>
<td>greenish-brown</td>
<td></td>
<td>2305</td>
</tr>
<tr>
<td>TiCl$_3$·3C$_6$H$_5$CH$_2$CN</td>
<td>blue-violet</td>
<td></td>
<td>2315</td>
</tr>
</tbody>
</table>

Stretching frequencies, $\nu$(C≡N), of uncoordinated nitrile ligands:

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\nu$(C≡N) cm$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CN</td>
<td>2253 cm$^{-1}$</td>
<td>[27, 28, 33]</td>
</tr>
<tr>
<td>CH$_2$:CHCN</td>
<td>2230 cm$^{-1}$</td>
<td>[29, 30]</td>
</tr>
<tr>
<td>C$_6$H$_5$CN</td>
<td>2229 cm$^{-1}$</td>
<td>[31, 33]</td>
</tr>
<tr>
<td>C$_6$H$_5$CH$_2$CN</td>
<td>2250 cm$^{-1}$</td>
<td>[32]</td>
</tr>
</tbody>
</table>

The diffuse reflectance spectra of the above-mentioned compounds are markedly different from those of distorted octahedral complexes of the type TiCl$_3$·3L (L = neutral ligand), characterized by a simple asymmetric absorption band in the visible region. The absorption bands in the diffuse reflectance spectrum of TiCl$_3$·CH$_3$CN found at 16 000 and 11 900 cm$^{-1}$ suggest the trigonal bipyramidal configuration of this compound [35, 36].

Infrared spectra of all the investigated compounds (Table 1) show an increase in the $\nu$(C≡N) stretching frequency, due to an increase in the CN force constant. The increase of the $\nu$(C≡N) frequency upon coordination has been attributed to increased $\sigma$-bond between the titanium(III) atom and CN group linked through the lone electron pair located at the nitrogen atom. Another acetonitrile vibration exhibiting a large shift upon coordination is the $\nu$(C—H) stretch which is observed to increase ca. 20 cm$^{-1}$ in the [TiCl$_3$(CH$_3$CN)$_3$]. In addition to this, [TiCl$_3$(CH$_3$CN)$_3$]·CH$_3$CN shows a less intensive $\nu$(C—C) stretch at 920 cm$^{-1}$ which indicates [16] that in the solid adduct a part of CH$_3$CN remains uncoordinated.
References


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