

Halo-complexes of Titanium(III): the Thermo-chromic Behaviour of [NBu₄][TiCl₄(thf)₂]

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Abstract

TiCl₃(thf)₃ reacts with ACl (A = NBu₄, PPN; PPN = Ph₃P=N=PPh₃) in dichloromethane solution, affording the compounds A[TiCl₄(thf)₂] (A = NBu₄, **1**; A = PPN, **2**). Compound **1**, dissolved in CH₂Cl₂, exhibits thermochromic behaviour which has been the subject of variable-temperature UV-VIS investigations.

Keywords: titanium(III), chloride, UV-VIS, thermochromism, ion pairs

Since titanium halides have been extensively used as precursors of Ziegler-Natta polymerization catalysts [1], their coordination chemistry has been widely explored [2]. Mono- and dinuclear chlorotitanates(IV) are easily prepared by addition of halide ions to neutral titanium tetrachloride, the nature of the products depending on the solvent and on the halide / Ti molar ratio employed [3]. As far as the chlorotitanate(III) species are concerned, the dinuclear [Ti₂Cl₉]³⁻ and the mononuclear [TiCl₆]³⁻ were prepared at high temperatures in the solid state [4]. On the other hand, the synthesis of the [TiX₄L_n]⁻ anions [X = Cl, Br; L_n = (thf)₂, dme; thf = tetrahydrofuran, dme = 1,2-dimethoxyethane] has been generally accomplished by halide addition to neutral Ti(III) derivatives [5]. Moreover, the complex-anion [TiCl₄(thf)₂]⁻ has been obtained *via* different pathways: *i*) chemical reduction of titanium(IV) precursors, either with M(η^6 -arene)₂ [M = Cr, Mo; arene = CH₃C₆H₅, 1,3,5-(CH₃)₃C₆H₃] [5b] or with CoCp₂ [Cp = η^5 -C₅H₅] [4c]; *ii*) photochemical reaction of [NBu₄]₂[TiCl₆] with visible light in thf solution [5d].

In the course of our investigations on the reactivity of early-transition metal compounds, we have found that [NBu₄][TiCl₄(thf)₂], **1**, forms by addition of NBu₄Cl to TiCl₃(thf)₃ in CH₂Cl₂ [6]. Interestingly, we noticed that the yellow-brown solution of **1** at room temperature turned pale-blue when it was cooled down by evaporation of the solvent *under vacuo*, finally affording a yellow-brown microcrystalline solid. Once this solid was dissolved again in dichloromethane, the resulting

solution was cooled down and turned pale-blue at ca. -60 °C. The cooling-warming cycle was repeated many times, observing always the same colour changes.

It is interesting to observe that a product very similar to **1**, *i.e.* the *blue* $[\text{NBu}_4][\text{trans-TiCl}_4(\text{thf})_2]\text{thf}$, was described by Sobota and coworkers [5d], but no indication of thermochromic behaviour, in solution as well as in the solid state, was reported. On the other hand, EPR analysis on a *blue* dichloromethane solution of **1**, frozen at 120 K, has shown a spectrum characterized by a orthorhombic symmetry (g values: 1.978, 1.897 and 1.777), in agreement with a *cis* configuration of the $[\text{TiCl}_4(\text{thf})_2]^-$ anion (Figure S1 given as Supplementary Material).

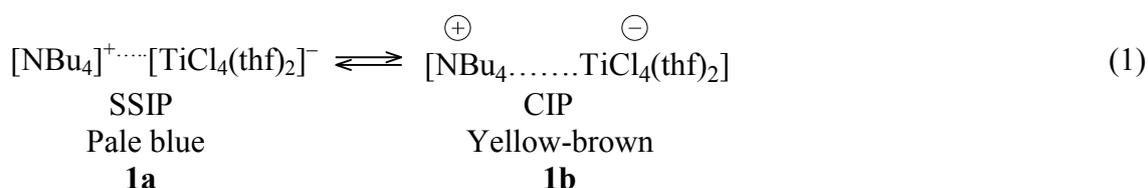
In order to attempt an explanation of the optical properties of the solutions of compound **1**, we decided to carry out UV-VIS spectra at different temperatures (see Figure 1). Thus, the UV-VIS spectrum in CH_2Cl_2 at room temperature displays two main absorptions at 475 and 720 nm. On lowering the temperature (Figure 1A, temperature decreasing from 1 to 8), the wavelength of the former absorption does not change, whereas its absorbance decreases. The dependence of the absorbance, related to the 475 nm absorption, on the temperature is plotted in Figure 2. Differently, the other band shifts progressively from 720 ($T = 26^\circ\text{C}$) to 660 nm ($T = -12^\circ\text{C}$), being the absorbance basically unchanged (Figure 1A). The trend observed in the UV-VIS spectra at temperatures higher than room temperature reflects what found at lower temperatures: the band at 475 nm increases in intensity on increasing the temperature, while the low-energy band shifts to higher wavelengths without substantial variation of the intensity (see Figure 1B, temperature increasing from 1 to 3).

Insert Figures 1 and 2 about here

Thermochromism behaviour, a reversible change in the colour of a compound when it is heated or cooled, can be the manifestation of different features, including changes in the crystalline phase (as is the case of tetraiodomercurate salts, $[\text{HgI}_4]^{2-}$ [7]), in the ligands geometry (as in $[\text{NEt}_4]_2[\text{CuCl}_4]$ [8]), or in the coordination number (as in $[\text{NEt}_4]_2[\text{NiCl}_4]$ [9]). In solution, when ion-pairs are

involved, the solvent itself may cause thermochromism by influencing the cation-anion interaction [10].

In view of the fact that compound **1** does not change colour when heated or cooled in the solid state, and that the octahedral coordination is the most common geometry adopted by the titanium(III) ion, the spectroscopic data discussed above could be interpreted admitting the occurrence in solution of the equilibrium (1) between solvent-separated ion pairs (SSIP), **1a**, and contact-ion pairs (CIP) **1b**.



Hence, the absorption at 475 nm may be assigned to a charge-transfer process from the anion to the cation, and the lower-energy absorption (660–720 nm) to a *d-d* transition on the titanium(III) ion [11], respectively. On increasing the temperature, the equilibrium shifts towards right, thus favouring the formation of **1b**, characterized by the charge-transfer band at 475 nm: the endothermic formation of ion pairs has been already observed in solutions of carbonylato anions $[\text{M}(\text{CO})_n]^-$ [12]. The enhanced cation-anion interactions within **1b**, which reduce the energy gap between the d-orbitals [11], are probably responsible of the shift toward higher wavelengths of the *d-d* transition absorption, observed on increasing the temperature.

The hypothesis that contact ion pairs are present in dichloromethane is supported by the fact that the charge-transfer band is almost absent in the UV-VIS spectrum of **1** in thf at room temperature (Figure 3). In fact, the major polarity of this solvent, with respect to CH_2Cl_2 , should largely favour the formation of SSIP species [13].

Insert Figure 3 about here

Compound **2** has been prepared from PPNCl by the same procedure described for **1** [14], and characterized by IR spectroscopy and elemental analysis. Interestingly, this light-green compound does not exhibit thermochromic behaviour in CH₂Cl₂ solution in the range of temperatures +30 ÷ – 78°C. This may be related to the larger steric hindrance of the PPN⁺ cation with respect to the [NBu₄]⁺ one. Coherently with the speculations above, such steric effects should disfavour the proximity of the ions, thus preventing the formation of ion pairs.

In conclusion, the Ti(III) derivative [NBu₄][TiCl₄(thf)₂], obtained from the combination of NBu₄Cl and TiCl₃(thf)₃ in CH₂Cl₂, shows thermochromic behaviour due probably to the establishment of contact ion pairs in solution at room temperature (absorption at 475 nm, yellow-brown colour). On decreasing the temperature, solvent-separated ion pairs become preponderant, thus the blue-green colour of the solution (associated with a *d-d* transition band) is observed.

Acknowledgements

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Supplementary material

Figure S1 reports the EPR spectrum of a frozen CH₂Cl₂ solution of [NBu₄][TiCl₄(thf)₂]. Supplementary data associated with this article can be found, in the online version, at [doi:.....](#)

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- [6] A colourless solution of NBu₄Cl (1.43 g, 5.15 mmol) in CH₂Cl₂ (50 ml) was treated with TiCl₃(THF)₃ (1.89 g, 5.10 mmol). The resulting yellow-brown mixture was stirred for 2 h at room temperature, then the volume of the resulting solution was reduced to *ca.* 10 ml. While removing the solvent under reduced pressure without heating, the colour of the solution turned pale-blue. The colour came back to yellow-brown when the solution was allowed to warm up to room temperature. Pentane (25 mL) was added, causing the precipitation of NBu₄[TiCl₄(THF)₂], **1**, as a microcrystalline pale yellow-brown solid. The latter was isolated by filtration and dried in vacuo at room temperature. Yield: 1.512 g, 52%. Anal. Calc. for C₂₄H₅₂Cl₄NO₂Ti: C, 50.01; H, 9.09; N, 2.43; Cl, 24.60; Ti, 8.31. Found: C, 49.84; H, 8.92; N, 2.33; Cl, 24.30; Ti, 8.12. IR (solid state): 2961s, 2874m, 1476m, 1458m, 1380m-w, 1263w, 1170w, 1151w, 1026m-s ($\tilde{\nu}_{\text{as}}$ O-CH₂), 858vs ($\tilde{\nu}_{\text{s}}$ O-CH₂), 728s, 697w cm⁻¹. $\chi_{\text{M}}^{\text{corr}} = 1.11 \times 10^{-3}$ cgsu; diamagnetic correction = 326×10^{-6} cgsu. μ_{eff} (290 K) = 1.61 BM.
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- [13] The low intensity of the highest-energy band is consequence also of the low solubility of the product.
- [14] Compound **2** was prepared by the same procedure described for **1**. [PPN][TiCl₄(THF)₂]: light green, 55%. Anal. Calc. for C₄₄H₄₆Cl₄NO₂P₂Ti: C, 60.57; H, 5.31; N, 1.61; Cl, 16.25; Ti, 5.49. Found: C, 60.66; H, 5.20; N, 1.50; Cl, 15.87; Ti, 5.52. IR (solid state): 3054w, 2963w, 2881w, 1587m, 1482m, 1393s, 1311m-w, 1300m, 1261m, 1188w, 1111s, 1020s ($\tilde{\nu}_{as}$ O-CH₂), 866vs ($\tilde{\nu}_s$ O-CH₂), 761m, 720s, 693m-s cm⁻¹.

Captions For Figures

Figure 1. UV-VIS spectrum of **1** in CH₂Cl₂ recorded at different temperatures. A) The traces refer to the following temperatures: 26 (trace 1), 21, 18, 14, 10, 7, 2, -12 (trace 8) °C. ([Ti]= 0.054 M). B) The traces refer to the following temperatures: 27 (trace 1), 29 (trace 2), 43 (trace 3) °C. ([Ti]= 0.01 M).

Figure 2. Variation of the absorbance at 475 nm with the temperature for **1** in CH₂Cl₂.

Figure 3. Comparison of the UV-VIS spectra of **1** in CH₂Cl₂ and thf at room temperature.