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Reaction of Titanocene Dichloride with Acetylenedicarboxylate

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Abstract

The reaction of Cp_2TiCl_2 with either the mono- or dipotassium salt of acetylenedicarboxylic acid (ADC) gives high yields of an insoluble orange product. The insoluble compound shows potential semiconductor behavior, as evidenced by an apparent bandgap in the orange region of the visible spectrum. Under N_2 , the compound decomposes at 238°C , eventually losing approximately 46% total mass up to 1350°C . The exothermic decomposition in air, beginning at 235°C , results in the formation of titanium oxides.

Introduction

Electron transfer between metal centers is important in many industrial and biological catalyst systems. To model these catalysts, Stephan and coworkers have prepared several early-late heterobimetallic (ELHB) compounds, with S and/or P atoms bridging the two metals (Stephan, 1989). Titanocene dichloride is often used as the electron deficient metal in these complexes. The challenge lies in finding new and diverse ligands that would make suitable candidates for the synthesis of novel multi-metal complexes. Either acetylene dicarboxylic acid (ADC), or acetylene dicarboxylic acid, monopotassium salt (KADC) meet these requirements. The structure of these ligands affords the potential for bridging two metal centers. Herein is reported the reaction of titanocene dichloride and potassium salts of acetylene dicarboxylic acid.

Materials and Methods

Reactions were carried out in air at ambient conditions. The dipotassium salt of ADC was prepared as described by Carraher (Williams, et al., 1989). All other reagents were used as purchased without further purification. Infrared spectra were obtained on a Nicolet 5PC FT-IR Spectrophotometer using KBr pellets or Nujol mulls on NaCl plates. X-ray diffraction patterns were acquired on a Rigaku D/MAX-B unit. Bandgap measurements were taken on a Perkin-Elmer Lambda 19 UV/VIS/NIR Spectrophotometer. For the bandgap measurements, the sample was prepared by suspending the orange powder

in acetone and brushing it onto a glass slide. An apparatus consisting of a Hewlett Packard 712B voltage supply, a Keithley 177 Digital Multimeter (DMM), and JDR Instruments DMM-300 Multimeter, was used to procure resistivity-conductivity measurements. Thermal gravimetric analyses were obtained on a Seiko TG/DTA 320 instrument. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN.

Reaction of Cp_2TiCl_2 with KADC

A 0.10 g (0.40 mmol) sample of Cp_2TiCl_2 , 0.06 g (0.39 mmol) KADC and 20 mL H_2O was stirred for several hours. The orange product began to precipitate out of the slurry after approximately 30 min. The reaction was considered complete when there was no longer any Cp_2TiCl_2 visible in the mixture. The orange powder, *I*, was filtered by suction filtration and washed with several portions of CH_3OH and water. Yield = 0.1086 g. Anal. found C, 56.41; H, 3.43; Ti, 15.60%. IR: 1635.84 (s), 1442.94 (m), 1298.26 (s), 1018.54 (m), 769.70 (m), 621.15 (m) cm^{-1} . X-ray Diffraction (d-spacings) (\AA): 6.328 (s), 5.805 (vs), 4.683 (m), 4.089 (w), 3.942 (m), 3.540 (w), 2.860 (w), 2.620 (w), 2.272 (w), 2.029 (vw), 1.789 (vw), 1.544 (vw).

Reaction of Cp_2TiCl_2 with K_2ADC

Method A. A 0.14 g (1.2 mmol) sample of ADC and a 0.14 g (2.4 mmol) sample of KOH were dissolved in 30 mL of H_2O to yield a clear colorless solution of K_2ADC . A 0.31 g (1.2 mmol) sample of Cp_2TiCl_2 was dissolved in 30 mL of CHCl_3 in a separate flask. The contents of the two flasks were combined and allowed to react by rapid stirring.

Method B. A 0.14 g (1.2 mmol) sample of ADC and a 0.14 g (2.4 mmol) sample of KOH were dissolved in 30 mL of H₂O to yield a clear colorless solution of K₂ADC. A 0.31 g (1.2 mmol) sample of Cp₂TiCl₂ was dissolved in 30 mL of CHCl₃ in a separate flask. The contents of the two flasks were combined and allowed to react by a much slower process of magnetic stirring. The resulting solution was allowed to stir for 10 minutes followed by diffusion of the layers for several days.

In both cases, the product (a yellow-orange powder) was recovered by suction filtration and washed with water and chloroform. IR: 1624.22 (s), 1442.94 (m), 1296.33 (s), 1033.98 (m), 769.70 (m), 623.45 (m) cm⁻¹. X-ray Diffraction (d-spacings) (Å): 6.308 (m), 5.804 (s), 4.680 (m), 4.090 (w), 3.931 (m), 3.532 (w), 2.851 (w), 2.622 (w), 2.261 (w), 2.045 (vw), 1.782 (vw), 1.536 (vw).

Results and Discussion

The orange product from the reaction of Cp₂TiCl₂ and KADC is easily obtained. The two reagents are allowed to stir in water in air at room temperature, and the powder is recovered by suction filtration. A slight excess of Cp₂TiCl₂ was used to insure complete reaction of KADC. This necessitated several washings with CH₃OH to remove excess Cp₂TiCl₂. The product was also washed with water to remove any KCl.

An alternate method for the synthesis of the orange product is similar to reactions of Carraher (Williams et al., 1989). In this method, K₂ADC, the dipotassium salt of the acid, is employed. The acid in the aqueous phase is allowed to come in contact with the organic phase containing the titanocene dichloride. This contact is accomplished either by stirring the layers with a rapid stirrer or stirring the layers for 5-10 minutes with a magnetic stirrer, then allowing the reaction to remain covered, undisturbed for several days. When chloroform is used as the organic solvent of Cp₂TiCl₂, a microcrystalline product is obtainable. Further attempts to grow larger crystals suitable for single crystal x-ray diffraction have been unsuccessful.

The reported time required for rapid stir techniques is on the order of sixty seconds (Williams et al., 1989). Rapid stir techniques for the reaction of Cp₂TiCl₂ and K₂ADC require considerably longer times for completion, often taking 15-30 minutes. Possible differences in reaction times may be due to the lower nucleophilicity of ADC ions or to solution pH. Carraher alters the pH of the carboxylic acid with additional base to a slightly basic solution (Williams et al., 1989). No attempts were made to control pH in any of our reactions. Fig. 1 shows the pH of the solution as a function of time for an aqueous

reaction of 0.3 g Cp₂TiCl₂ with 0.18 g KADC in 30 mL of H₂O. The pH of the solution drops rapidly with the addition of KADC and continues to drop exponentially with time.

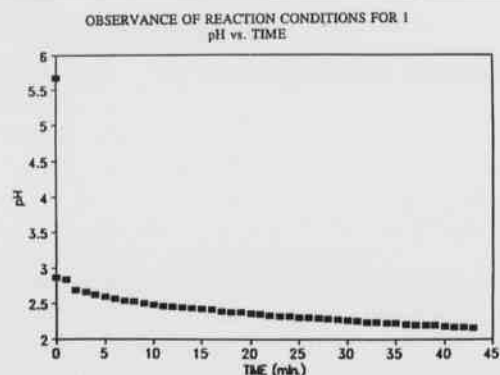


Fig. 1. Plot of pH vs. time for the reaction of Cp₂TiCl₂ with KADC.

The orange products from either method are not soluble in any common solvent or solvent systems. The products react with N,N-dimethylformamide (DMF), pyridine, and hydrochloric acid. Characterization of the products obtained from the reactions with DMF and pyridine are still underway. The addition of HCl to the orange powder reforms the starting material, Cp₂TiCl₂. The insolubility of the adc compounds precludes molecular weight determination. Carraher and Lee (1975) have reported the formation of polymers from the reaction of Cp₂TiCl₂ with salts of diacids. Some of their products were also insoluble and could not be further characterized. The soluble polyesters had average molecular weights of 3 x 10⁵ g/mol. These results suggest that the orange products formed from Cp₂TiCl₂ and ADC salts are also insoluble polyesters. The IR data indicates a chelated ester stretch at 1625-1635 cm⁻¹. R.N. Kapoor et al., (1987) have reported the structure of a titanocene complex in which the titanium atom has two chelated esters as ligands.

Because the two products from the two separate synthetic methods had observably different orange colors they were analyzed to see if the two methods gave dissimilar products. The decomposition points of the materials using a Mel-temp apparatus are 235° C for the reaction with KADC and 190° C for the reaction with K₂ADC. Singly, this indicates two distinct products. However, X-ray diffraction patterns (Fig. 2) and infrared spectra show conclusively that the two products are identical in structure. The difference in color and decomposition point suggests a difference in chain length of a polymer.

A thermal gravimetric analysis (TGA) of the Cp₂TiCl₂/KADC product under N₂ shows a small mass loss at approximately 70° C (Fig. 3). The compound

begins rapid decomposition at 238° C. This initial 14% mass loss is associated with a large exotherm. Calculations based on mass loss indicate possible loss of one CO₂ per acetylenedicarboxylate ligand. The TGA exhibited almost continual loss of material up to 1350° C, losing a total of 46% of its mass. The TGA of the Cp₂TiCl₂/KADC product in air (Fig. 4) shows a small mass gain before decomposition at 235° C. A second mass increase of 1.2% occurs before the burning off of the organic fragments to a final total mass loss of 69.8%. This percentage remaining would be consistent with the formation of TiO₂.

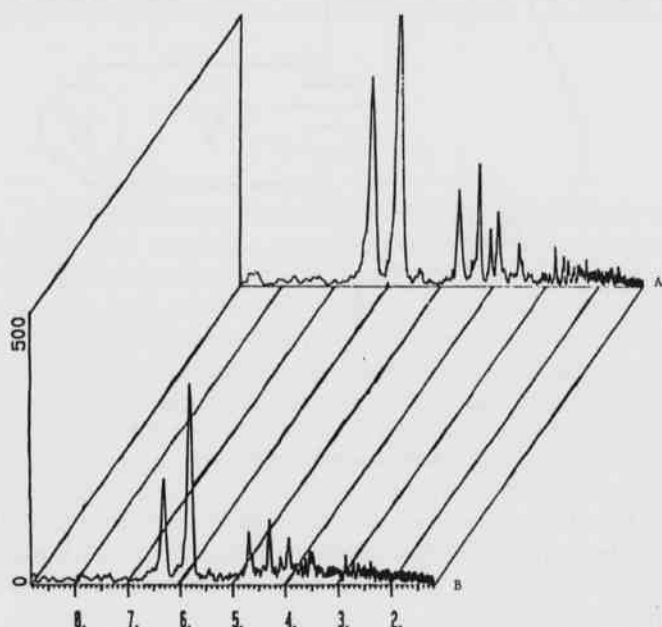


Fig. 2. X-ray diffraction patterns for A) Cp₂TiCl₂/KADC product and B) Cp₂TiCl₂/K₂ADC product.

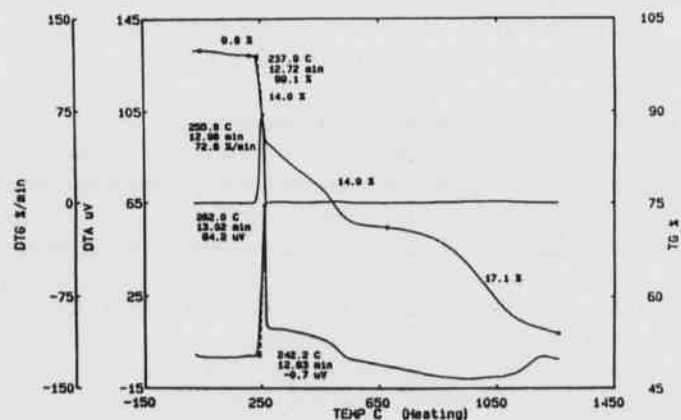


Fig. 3. Thermal gravimetric analysis in N₂ of the orange product from the reaction of Cp₂TiCl₂ with KADC.

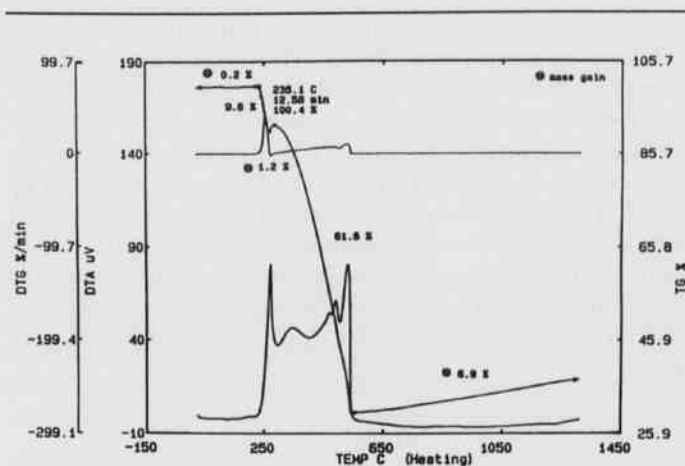


Fig. 4. Thermal gravimetric analysis in air of the orange product from the reaction of Cp₂TiCl₂ with KADC.

An X-ray diffraction pattern of Cp₂TiCl₂/KADC sample after thermal decomposition in air was computer matched to several different titanium oxide phases. While none of the phases were exact matches, most were close enough to indicate the decomposed material is a titanium oxide of unknown stoichiometry.

An optical absorbance vs. wavelength spectrum of the Cp₂TiCl₂/KADC product is shown in Fig. 5. The data indicated a transmittance window from 875-600 nm. The rapid increase in absorbance near 600 nm results from electron transitions from the valence band to the conduction band as photons are absorbed. Absorbance spectra of this type are typical of semiconducting materials. The spectrum indicated a bandgap of approximately 2.1 eV. Considering the narrow transmittance window, a possible application of 1 may be as an optical bandpass filter. The absorption in the portion of the spectrum from 3200-875 nm results from a combination of bond-resonance and intraband free carrier absorption. It is possible to observe the bond-resonance absorptions because these wavelengths make up the near-infrared (NIR) portion of the spectrum.

The electrical resistivity was determined through straightforward electrical resistance measurements for pressed pellets of diameter 28 mm and thickness approximately 3 mm. Resistance was determined by application of voltage up to a maximum of 500 V DC between silver ink contacts applied to the faces of the pellets, measurement of current through the pellets via a standard ammeter and use of Ohm's Law:

$$R = V/I \text{ and } \rho = RA/l = 1/\sigma, \text{ where}$$

ρ is the resistivity in ohm-cm, R the resistance in ohms, A the cross sectional area of the face, l the thickness, and σ the conductivity in (ohm-cm)⁻¹. Resistivity measurements

yielded a linear relationship between current and voltage. This can be seen from Fig. 6. The resistivity, ρ , of the orange K_2ADC/Cp_2TiCl_2 product, I , is approximated by $\rho = Vwt/Il$. The symbols w , t , and l are dimensions of the sample. Voltage and current are denoted by V and I , respectively. A diagram of this apparatus is presented in Fig. 7. The resistivity of I is 2.86×10^7 ohm-cm. Although very simple, this measurement scheme was rapid, convenient, and satisfactory for "order-of magnitude" estimates as required in this preliminary study. Further research is needed to explore all possible applications of this material.

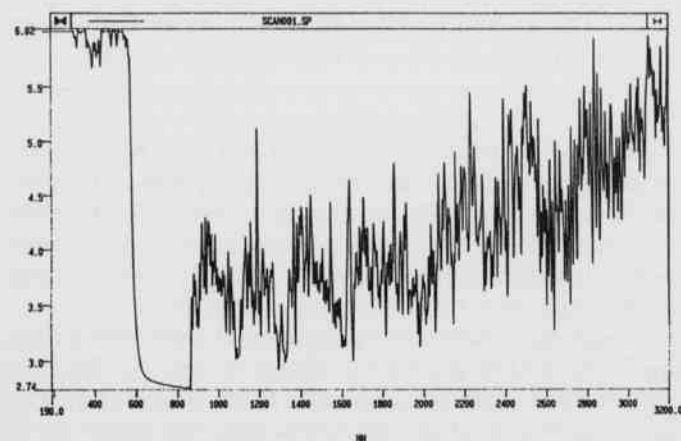


Fig. 5. Optical absorbance spectrum of the orange product from the reaction of Cp_2TiCl_2 with KADC.

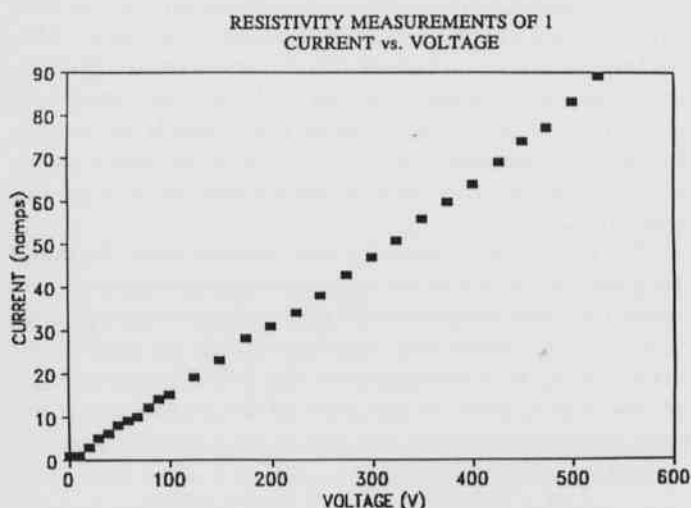


Fig. 6. Resistivity measurements of the orange product from the reaction of Cp_2TiCl_2 with KADC.

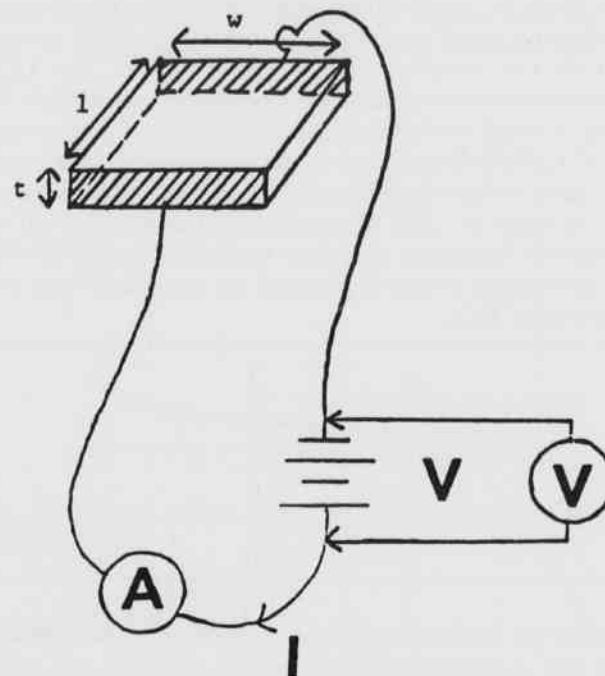


Fig. 7. Diagram of the resistivity apparatus.

Acknowledgements

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