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Microwave Syntheses and Thermal Gravimetric Analysis of *trans*-Hydrogen bis(dimethylsulfoxide)tetrachlororuthenate(III)

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The $Ru(dmso)_2Cl_4^-$ anion has been prepared by the reaction of $RuCl_3$ with HCl in dimethyl sulfoxide (DMSO) at elevated temperatures (Alessio et al. 1991). The successful microwave synthesis of $RuCl_2(dmso)_4$ (Harvey et al. 2009) led us to explore the use of microwave technologies for improving the synthesis of *trans*-$[H(dmso)_2][Ru(dmso)_2Cl_4]$.

The starting material, $RuCl_3 \cdot xH_2O$, ethanol, aqueous HCl and dimethyl sulfoxide were purchased from Aldrich Chemical Company. All reagents were used as purchased without further purification. An Agilent 8453 UV-Visible spectrophotometer was used for the analysis of the compounds. Thermal analysis was done on a Seiko DT/TGA 320 Thermoanalyzer under Ar gas (300ml/min) with copper reference and sample pans. The sample of *trans*-$[H(dmso)_2][Ru(dmso)_2Cl_4]$ (8.252 mg) was heated from 30 – 350 ^oC at 5 ^oC/min. The microwave synthesis was performed using a CEM Discover Microwave Reactor. ^1H NMR spectra were obtained on a Bruker Avance 300 NMR spectrophotometer using *d*-chloroform with TMS as an internal standard.

Three methods were employed for the microwave synthesis of *trans*-$[H(dmso)_2][Ru(dmso)_2Cl_4]$:

Method A: A 0.15 g (0.57 mmol) sample of $RuCl_3 \cdot xH_2O$ was dissolved in 0.7 mL DMSO and 0.1 mL 37% aqueous HCl, and the mixture was placed in the microwave reactor and heated to 80 °C for 2 min. A red-orange solution was obtained and after addition of 5 mL acetone and setting for several hours at room temperature, red crystals formed. The product was filtered, washed with acetone and vacuum dried; yield = 95 %, melting point (mp) = 120 ^oC.

Method B: A 0.10 g (0.38 mmol) sample of $RuCl_3 \cdot xH_2O$ was placed in the microwave reaction tube with 2 mL ethanol, and the mixture was heated in the microwave reactor to 75 °C for 15 min. Then 0.2 mL DMSO and 0.1 mL 37% aqueous HCl was added and the mixture was heated in the microwave to 75 °C for 3 min. The resulting red-orange solution formed red crystals after addition of acetone and leaving for several hours at room temperature. The product was filtered, washed with acetone and vacuum dried; yield = 79 %, mp = 120 ^oC.

Method C: The reaction was done by placing the four reagents, 0.10 g (0.38 mmol) $RuCl_3 \cdot xH_2O$, 0.2 mL DMSO, 0.1 mL 37% aqueous HCl, and 2 mL ethanol together in the reaction tube and the mixture was heated in the microwave reactor to 75 °C for 18 min. After the 18 min reaction time, a red-orange color formed in the solution. After addition of acetone, and leaving for several hours at room temperature, red crystals precipitated from solution. The product was filtered, washed with acetone and vacuum dried; yield = 67 %, mp = 120 ^oC.

The visible spectrum (Figure 1) and melting points of the products from all three microwave methods matched the literature values for *trans*-$[H(dmso)_2][Ru(dmso)_2Cl_4]$ (Alessio et al. 1991). Proton NMR spectra of the products obtained from the microwave reactions were identical to the NMR spectrum obtained for *trans*-$[H(dmso)_2][Ru(dmso)_2Cl_4]$ prepared following the methods of Alessio and coworkers (Alessio et al. 1991).

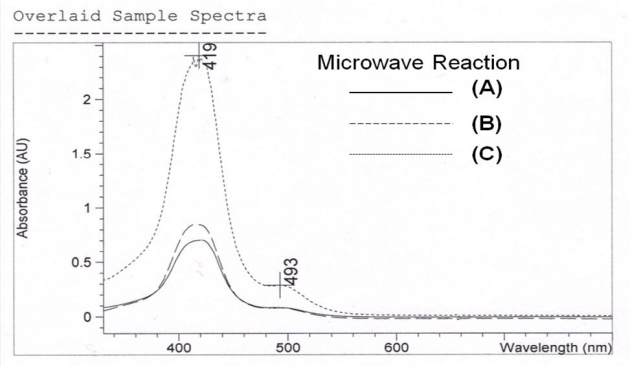

Figure 1. Visible spectra of *trans*-$[H(dmso)_2][Ru(dmso)_2Cl_4]$ prepared using microwave techniques.

Microwave synthesis of *trans*-$(Ph_4P)[Ru(dmso)_2Cl_4]$, Ph = phenyl

A 0.15 g (0.57 mmol) sample of $RuCl_3 \cdot xH_2O$ was dissolved in 0.7 mL DMSO and 2 mL ethanol, and

0.22 g (0.57 mmol) Ph_4PCl (tetraphenylphosphonium chloride) was added. The mixture was placed in the microwave reactor and heated to 100 °C for 2 min. Upon reaction completion, an orange precipitate formed. The product was filtered and dried; yield = 54 %, mp = 120 °C. The visible spectrum matched the values reported in the literature for *trans*-$[H(dmso)_2][RuCl_4(dmso)_2]$ (Alessio et al. 1991).

Microwave Syntheses. Three methods for the microwave synthesis of the title compound were investigated. The first two microwave methods mirrored the preparations reported in the literature (Alessio et al. 1991). Microwave Method C varies from Method A by the addition of ethanol. Ethanol was used by Alessio to improve solubility of the $RuCl_3$ before reaction with DMSO.

The microwave techniques provide a possible alternate preparative route for the synthesis of *trans*-$[H(dmso)_2][Ru(dmso)_2Cl_4]$. Method A (95 % yield) gave a better yield than the literature preparation (80%). Method B showed a comparable yield to that reported in the literature and Method C had a lower yield than the literature (Alessio et al. 1991). In particular, method A provides the best synthetic route for the title compound as seen by the increase in yield and the decrease in reaction times (2 min vs 30 min).

Addition of PPh_4Cl as a chloride source also provided a counterion for the $Ru(dmso)_2Cl_4^-$ ion. Though lower yields are obtained, *trans*-$PPh_4[Ru(dmso)_2Cl_4]$ precipitates from solution and can easily be isolated.

Thermal Analysis of *trans*-$[H(dmso)_2][Ru(dmso)_2Cl_4]$. The thermal decomposition of *trans*-$[H(dmso)_2][Ru(dmso)_2Cl_4]$ can be seen in Figure 2. With an onset temperature of 108.4 °C, the *trans*-$[H(dmso)_2][RuCl_4(dmso)_2]$ complex decomposes in five steps, starting with the initial loss of HCl. Subsequent loss of the four remaining DMSO moieties occurs in a stepwise manner. Thermal decomposition of *trans*-$[H(dmso)_2][Ru(dmso)_2Cl_4]$ occurs between 100 and 300 °C as the title compound loses mass stepwise until $RuCl_3$ remains. Understanding the thermal properties of *trans*-$[H(dmso)_2][Ru(dmso)_2Cl_4]$ may lead to improved syntheses of other Ru(III) complexes (Alessio et al. 1991).

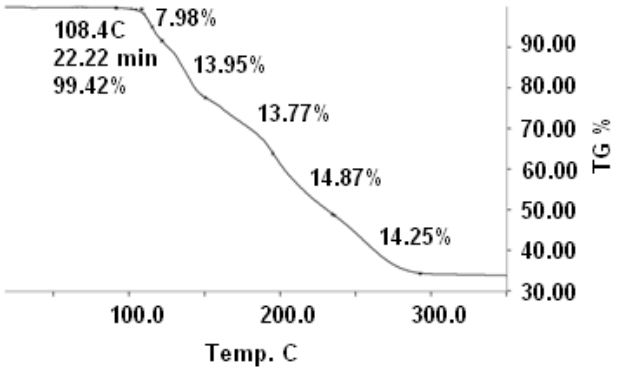

Figure 2. Thermal Gravimetric Analysis plot for *trans*-$[H(dmso)_2][Ru(dmso)_2Cl_4]$

Acknowledgments

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