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Properties and one-step synthesis of (2-acetylpyridine)tetraammineruthenium(II), $[Ru^{II}(2\text{-acpy})(NH_3)_4]^{2+}$ and tetraammine(2-benzoylpyridine)ruthenium(II), $[Ru^{II}(NH_3)_4(2\text{-bzpy})]^{2+}$ Redox potentials, UV–Vis and NMR spectra☆

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Abstract

A more direct and efficient route to the syntheses of $[Ru(NH_3)_4(X\text{–}Y)](BF_4)_2$, where X–Y can be 2-acetylpyridine (2-acpy) or 2-benzoylpyridine (2-bzpy), based on the reactions of $[RuCl(NH_3)_5]Cl_2$ with these *ortho*-substituted azines is described. The $[Ru(2\text{-acpy})(NH_3)_4](BF_4)_2$ and $[Ru(NH_3)_5(2\text{-bzpy})](BF_4)_2$ complexes have a molar conductance of 328 and 292 $\Omega^{-1}\,cm^2\,mol^{-1}$, respectively, corresponding to a 1:2 species in solution. These complexes showed two intense absorption bands around 620–650 and 380 nm, the energies of which are solvent dependent, decreasing with the increase of the Gutman's donor number of the solvent, and were assigned as metal-to-ligand charge transfer (MLCT). The complexes have oxidation potentials ($Ru^{II/III}$) of +0.380 V vs. Ag/AgCl (2-acpy) and +0.400 V vs. Ag/AgCl (2-bzpy), and reduction potentials ($X\text{–}Y^{0/-}$) of −1.10 V vs. Ag/AgCl (2-acpy) and −0.950 V vs. Ag/AgCl (2-bzpy) on $CF_3COOH/NaCF_3COO$ at pH=3.0, scan rate 100 mV s^{-1}, [Ru]=1.0×10^{-3} mol l^{-1}. Both processes show a coupled chemical reaction. Upon oxidation of the metal center, the MLCT absorption bands are bleached and restored upon subsequent reduction. In order to confirm the structure of the complexes a detailed ^1H NMR investigation was performed in d_6-acetone. Further confirmation of the structure was obtained by recording the ^{15}N NMR spectrum of $[Ru(NH_3)_4(2\text{-bzpy})]^{2+}$ in d_6-DMSO using the INEPT pulse sequence improving the sensitivity of ^{15}N by polarization transfer from the protons to the ^{15}N. The Nuclear Overhauser Effect (NOE) experiments were made qualitatively for $[Ru(NH_3)_4(2\text{-acpy})]^{2+}$, and showed that H_6 of the pyridine is close to a NH_3 proton, which should then be in a *cis* position, and, hence, confirming that acpy is acting as a bidentate ligand. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Rutheniumtetraammine; Inert ammonias; ^{15}N NMR

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1. Introduction

cis-$[RuCl_2(NH_3)_4]Cl$ is widely used as the starting material for *cis*-tetraammineruthenium complexes, including bidentate, but in particular for monodentate ligands [1]. *cis*-$[RuCl_2(NH_3)_4]Cl$ is usually synthesized from $[RuCl(NH_3)_5]Cl_2$ [2] through several steps, which are time consuming, and, hence, result in relatively low net yields. Alternative routes to the synthesis of *cis*-$[RuCl_2(NH_3)_4]Cl$ complexes have also been proposed [3–5]. On the other hand, $[RuCl(NH_3)_5]Cl_2$ is widely known as the starting material for ruthenium(II) pentaammines, $[Ru(NH_3)_5L]^{n+}$ [6]. However, as far as we know, the first example that $[Ru(NH_3)_5(H_2O)]^{2+}$ (generated by reduction of $[RuCl(NH_3)_5]^{2+}$) can react with a bidentate ligand to result in a *cis*-tetraammineruthenium(II) complex, is the reaction with 2-pyridinecarboxyaldehyde (pyC(O)H), which displaces the relatively inert *cis* ammines to yield $[Ru(NH_3)_4(pyC(O)H]^{2+}$ [7]. This type of reaction was

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eventually used to synthesize *cis* complexes skipping the *cis* dichloro complex synthesis, such as in Ru-flavin [8]. The current paper describes the synthesis of $[Ru(NH_3)_4(X–Y)]^{2+}$ {X–Y=2-acetylpyridine (2-acpy) or 2-benzoylpyridine (2-bzpy)} using two methods, one starting from $[RuCl(NH_3)_5]Cl_2$ and the other from *cis*-$[RuCl_2(NH_3)_4]Cl$. The yields from the two synthetic methods routes were determined and the products compared by elemental analysis, UV–Vis and IR spectra. To confirm the structures and stereochemistry of the one-step product a detailed NMR investigation was performed. In addition, the electrochemical behavior of the $[Ru(NH_3)_4(X–Y)]^{2+}$ complexes was investigated by cyclic voltammetry, including dependence of the observed peaks on the potentials range, scan rates, pH and medium used.

2. Experimental

2.1. Chemicals and reagents

Ruthenium trichloride '$RuCl_3 \cdot 3H_2O$' (Strem) was the starting material for the ruthenium complexes syntheses. 2-benzoylpyridine (2-bzpy) (Sigma) was used as supplied. 2-acetylpyridine (2-acpy) (Aldrich) was distilled twice before use. Sodium tetrafluoroborate (Aldrich) was recrystallized from hot water. Ether and acetone were distilled before use. All other reagents were reagent grade and used as supplied. Doubly distilled water was used throughout this work.

2.2. Syntheses

$[RuCl(NH_3)_5]Cl_2$: This starting complex was synthesized following a described procedure [9]. The average yield was 75%.

cis-$[RuCl_2(NH_3)_4]Cl$: This was synthesized following a described procedure [2]. The average yield was 45%.

$[Ru(NH_3)_4(X–Y)]Z_2$ (X–Y=acpy or bzpy; Z=BF_4^- or PF_6^- were prepared by two different methods. Method A, via $[RuCl(NH_3)_5]Cl_2$: 200 mg (0.68 mmol) of $[RuCl(NH_3)_5]Cl_2$ were added to 3 ml of a deaerated solution of CF_3COOH (pH=3.0), and gently warmed to help dissolution, and, then, Zn/Hg was added at room temperature. The mixture became a golden light brown solution, when $[RuCl(NH_3)_5]^{2+}$ is reduced. The solution (with Zn/Hg) was filtered over Zn/Hg. Argon was continuously bubbled through the filtrate, to which a slightly larger than equivalent amount of ligand was added (0.1 ml (0.89 mmol) of acpy, or 150 mg (0.82 mmol) of bzpy, in 4 ml of deaerated methanol). During the ligand addition, the color of the mixture turns to deep blue. The reaction was allowed to proceed with argon bubbling for 2 h, in the dark. The compound was isolated by the addition of a freshly prepared, filtered, deaerated, almost saturated aqueous solution (0.1 g ml^{-1}) of $NaBF_4$ or NH_4PF_6. The mixture was left under vacuum in the refrigerator, and the formed solid was collected by filtration, washed with ether and, then, vacuum dried. Recrystallization was made by dissolving the compound in deaerated acetone followed by precipitation with deaerated ether. Yields average 50% (calculated from $[RuCl(NH_3)_5]Cl_2$). Method B, via *cis*-$[RuCl_2(NH_3)_4]Cl$, following a described procedure [7] with slight modifications. 200 mg (0.72 mmol) of *cis*-$[RuCl_2(NH_3)_4]Cl$ (prepared from $[RuCl(NH_3)_5]Cl_2$) were added to 3 ml of a deaerated solution of CF_3COOH (pH=3.0), and gently warmed to help dissolution, and, then, Zn/Hg was added at room temperature. The mixture became a golden light brown solution, when $[RuCl(NH_3)_5]^{2+}$ is reduced. The solution (with Zn/Hg) was filtered over Zn/Hg. Argon was continuously bubbled through the filtrate, to which a slightly larger than equivalent amount of ligand was added (0.1 ml (0.89 mmol) of acpy or 150 mg (0.82 mmol) of bzpy in 6 ml of deaerated methanol). During the ligand addition, the color of the mixture turns to deep blue. The reaction was allowed to proceed with argon bubbling for 2 h, in the dark. The compound was isolated by the addition of a freshly prepared, filtered, deaerated, almost saturated aqueous solution (0.1 g ml^{-1}) of $NaBF_4$ or NH_4PF_6. The mixture was left under vacuum in the refrigerator, and the formed solid was collected by filtration, washed with ether and, then, vacuum dried. Recrystallization was made by dissolving the compound in deaerated acetone followed by precipitation with deaerated ether. Average yields were 32% (calculated from $[RuCl(NH_3)_5]Cl_2$).

2.3. Elemental analysis

Carbon, hydrogen and nitrogen microanalyses were performed in the Instituto de Química da Universidade de São Paulo. $[Ru(NH_3)_4(2\text{-bzpy})](BF_4)_2$ (synthesized via Method A): Calcd.: C, 27.32; N, 13.28; H, 4.02. Found: C, 26.67; N, 12.96; H, 3.99. $[Ru(NH_3)_4(2\text{-bzpy})](BF_4)_2$ (synthesized via Method B): Calcd.: C, 27.32; N, 13.28; H, 4.02. Found: C, 27.11; N, 13.32; H, 3.79. $[Ru(NH_3)_4(2\text{-acpy})](PF_6)_2$ (synthesized via Method A): Calcd.: C, 14.49; N, 12.07; H, 3.31. Found: C, 14.25; N, 11.50; H, 3.22. $[Ru(2\text{-acpy})(NH_3)_4](BF_4)_2 \cdot H_2O$ (synthesized via Method B): Calcd.: C, 17.45; N, 14.53; H, 4.39. Found: C, 17.01; N, 13.72; H, 4.18.

2.4. Electronic and NMR spectra

Electronic spectra were recorded on a Varian 634-S, a Cary 2200 or a HP 8452A UV–Vis spectrophotometer. All spectra were taken in an argon atmosphere, in a quartz cell of 1.0 cm path length. NMR spectra were recorded in model DPX 300 Bruker and WH400 Bruker NMR spectrometers. All the samples were dissolved in d_6-acetone or d_6-DMSO.