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Inorganica Chimica Acta 247 (1996) 129–130

Inorganica Chimica Acta

Note

Syntheses of *cis*- and *trans*-tetraamminedichlororuthenium(III) chloride

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Received 11 July 1995

Abstract

The syntheses of the salts *cis*- and *trans*-tetraamminedichlororuthenium(III) chloride are reported. The two isomers are precursors to a number of di-substituted ruthenium(II) and (III) complexes.

Keywords: Ruthenium complexes; Ammine complexes; Geometrical isomers

1. Introduction

We have repeatedly answered requests for a written description of the synthesis of *cis*- and *trans*-tetraamminedichlororuthenium(III) chloride [1]. These compounds are used in the syntheses of numerous other tetraammine ruthenium(III) and (II) complexes [2]. The original syntheses were reported by Gleu and Breuel [3] and Vogt et al. [4], however our procedures appear to be subtly different and provide convenient and reliable methods that other groups have found quite useful. Although used in this laboratory for more than 25 years, our synthetic procedures have not been previously published except in reference. Pell and Armor [5] also adapted the original synthesis by Gleu and Breuel for the *cis* isomer which closely follows our procedure. An alternative synthesis of the *cis* isomer involves the use of a catechol [6]. Recently, in a footnote, Sugaya and Sano [7] claim that there are some impurities in the latter method. Described here are the syntheses of *cis*- and *trans*-$[Ru(NH_3)_4Cl_2]Cl$ which have proven reproducibly useful in this laboratory.

2. Experimental

2.1. *Synthesis of cis-tetraamminedichlororuthenium(III) chloride (cis-[Ru(NH$_3$)$_4$Cl$_2$]Cl)*

Pentaamminechlororuthenium(III) dichloride (1.0 g, 0.0034 mol) was refluxed in deaerated concentrated ammonium hydroxide (25 ml) under a blanket of argon until the solution turned dark pink. A stoichiometric amount of sodium dithionate (0.70 g, 0.0034 mol) was then added to the hot solution from which, upon stirring in an ice bath, precipitated pentaaminehydroxoruthenium(III) dithionate. Addition of 100% ethanol completely precipitated the salt (1.2 g) which was filtered and air dried. The off-white salt was dissolved in a saturated solution of oxalic acid dihydrate (12 ml), and the mixture was refluxed under argon for about 5 min until a yellow solid precipitated and the mother liquor turned brown. The mixture was cooled and the yellow *cis*-tetraammine(oxalato)ruthenium(III) dithionate was collected by filtration and washed with ethanol. This product was dissolved in 5 N HCl (24 ml) and heated for about 10 min. After filtration, 100% ethanol (50 ml) was added to the yellow filtrate, precipitating the mustard colored solid. This material was cooled, filtered, washed with ethanol and air dried. Yield based on $[Ru(NH_3)_5Cl]Cl_2$ was 0.71 g (75%).

2.2. *Synthesis of trans-tetraamminedichlororuthenium(III) chloride (trans-[Ru(NH$_3$)$_4$Cl$_2$]Cl*

Pentaamminechlororuthenium(III) dichloride (2.00 g, 0.0068 mol) was dissolved in water (75 ml) at 78–85 °C. To this solution was added sodium bisulfite (2.84 g, 0.027 mol). Sulfur dioxide was slowly bubbled through the solution which was kept at 75 °C on a water bath. After about 15 min, faint yellow crystals started to form. These conditions were maintained for 1 h, after which the system was cooled with continued saturation of SO_2. The crystals were collected by filtration, washed with water and methanol and vacuum dried at room temperature. The yield of *trans*-$[Ru(NH_3)_4(HSO_3)_2]$ was 1.90 g (84%).

This product was dissolved in 6 N HCl (200 ml) by heating at the boiling point for 15 min. The reddish brown

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SSDI 0020-1693(95)04838-1

colored solution was cooled yielding crystals of *trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$. These were collected by filtration, washed with 6 N HCl and methanol and vacuum dried at room temperature. Yield: 1.35 g (77%).

The solid *trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$ was dissolved in a minimum of 1.5 N HCl (75 ml) and $HICl_2$ solution (7 ml) (prepared by addition of 1 ml of iodine monochloride to 6 ml of 6 N HCl) was slowly added dropwise to the hot solution. An orange salt precipitated when the solution was cooled. The solid product was collected by filtration, washed with ethanol, and air dried giving 1.80 g (93%) of *trans*-$[Ru(NH_3)_4Cl_2][ICl_2]$.

This solid was then added to a solution of sodium bisulfite (1.2 g) in water (5 ml) containing 1 ml of 12 N HCl to give a dark yellow compound. The solid product was collected by filtration, washed with a mixture of acetone and ethanol, then recrystallized from hot 0.02 N HCl. The orange crystals of *trans*-$[Ru(NH_3)_4Cl_2]Cl$ were separated by filtration, washed with ethanol and air dried. Overall yield based on starting $[Ru(NH_3)_5Cl]Cl_2$ was 1.03 g (54%).

2.3. Spectral characteristics

Chaisson et al. [8] have published the spectra of the *cis* and *trans* isomers. The spectrum of *cis*-$[Ru(NH_3)_4Cl_2]Cl$ has previously been published by Hartman and Bushbeck [9]. Briefly the absorption spectra in aqueous solution are dominated by the ligand-to-metal charge transfer bands with λ_{max} at 350 nm ($\epsilon = 1.5 \times 10^3$ M^{-1} cm^{-1}), 308 nm ($\epsilon = 1.3 \times 10^3$ M^{-1} cm^{-1}) and 260 nm sh ($\epsilon = 500$ M^{-1} cm^{-1}) for the *cis*-$[Ru(NH_3)_4Cl_2]Cl$ and at 331 nm ($\epsilon = 5.0 \times 10^3$ M^{-1} cm^{-1}) and 295 nm sh ($\epsilon = 710$ M^{-1} cm^{-1}) for the *trans*-$[Ru(NH_3)_4Cl_2]Cl$.

3. Summary

These tetraammine ruthenium(III) precursors provide the means to a wide variety of substituted ruthenium compounds. For example, aqueous solutions of either isomer can be reduced over amalgamated zinc in the presence of excess ligand to give the respective $Ru(NH_3)_4L_2^{2+}$ ions with high stereospecificity [10,11]. The convenient synthesis of these precursors in high yields is essential for the preparation of a variety of substituted complexes [12–15]. As noted above, the syntheses of the *cis* and *trans* dichloro complexes are not original, but our descriptions of these have proved useful to others. Although an alternative procedure for the synthesis of the *cis* isomer has been described [6], in our hands and apparently in the hands of others [12–14], the one described in the present article has given better yields of the purified materials with similar levels of effort.

Acknowledgements

Research in this laboratory is sponsored by the US National Science Foundation.

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