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The Synthesis of Dichlorobis(2,2′-bipyridyl)ruthenium(II)

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A new synthesis of cis-*[Ru(bipy)$_2$Cl$_2$] is presented, starting from [Ru(bipy)py$_4$]$^{2+}$. Also, a method for obtaining* cis–trans *mixtures of [Ru(bipy)$_2$Cl$_2$] is described. During conversion of* trans-*[Ru(bipy)$_2$py$_2$]$^{2+}$ to [Ru(bipy)$_2$Cl$_2$] isomerization is found to occur.*

Introduction

In 1963 Dwyer's group reported the synthesis of [Ru(bipy)$_2$Cl$_2$] (bipy = 2,2′-bipyridyl) by the pyrolysis of (bipyH)[Ru(bipy)Cl$_4$] [1]. It was assumed that the reaction produced only the *cis* isomer. This complex is rather important in that it is the starting point in a number of preparations and undoubtedly will continue to be important considering the current activity in ruthenium(II) chemistry.

We have repeated the Dwyer synthesis a number of times, and while we obtain a complex appearing to be "authentic" it is frequently not possible to reproduce other syntheses using it as a starting material. This has caused us to seek a better route to [Ru(bipy)$_2$Cl$_2$].

Our recent work with [Ru(bipy)py$_4$]$^{2+}$ [2] (py = pyridine) suggested a different route for this synthesis to us. Furthermore, we were able to prepare both *cis* and *cis–trans* mixtures of [Ru(bipy)$_2$Cl$_2$]. These results are reported here.

Experimental

Reagents

Unless otherwise specified chemicals were of reagent quality. 2,2′-Bipyridyl was obtained from Aldrich; RuCl$_3$3H$_2$O was from J. Bishop & Co.

Measurements

Infrared spectra were obtained on a Perkin-Elmer Model 283. Analyses were by Baron Consulting, Orange, Ct. 06477.

cis-*Dichlorobisbipyridylruthenium(II), [Ru(bipy)$_2$Cl$_2$]*

A stock solution of [Ru(bipy)py$_4$]$^{2+}$ was prepared as described earlier [2]. Two hundred ml of this solution (from 2.00 g [Ru(bipy)Cl$_3$] – (earlier incorrectly called [Ru(bipy)Cl$_4$]) was evaporated to dryness and mixed with 50 ml water, 10 ml ethanol, and 0.86 g bipy. After 2 hr on the steam bath this solution was mixed with 20 ml conc HCl, 5 ml ethanol, and boiled with stirring for 30 minutes. The black solid was isolated by filtration and washed with water; it consists of *cis* and *trans* isomers and occasionally a polymeric complex. Addition of the wet complex to 70 ml water, 20 ml ethanol and 4 ml pyridine, followed by 17 hr reflux gave an orange solution of [Ru(bipy)$_2$py$_2$]$^{2+}$; precipitation of an aliquot of this solution as the perchlorate showed the presence of both isomers (infrared spectrum [2]) but with considerably less *trans* than present initially. [*Caution*: these perchlorates can detonate on dry grinding].

The dichloro-complex is again precipitated by adding 30 ml conc HCl and boiling for 1 hr. After isolation it is converted to the bis-pyridine complex again by refluxing for 17 hr in 70 ml water, 20 ml ethanol and 4 ml pyridine. An aliquot of this solution shows essentially none of the *trans*-isomer. Final precipitation of [Ru(bipy)$_2$Cl$_2$] is achieved by adding 30 ml conc HCl and boiling for 1 hr; on cooling the product is washed with water and dried *in vacuo* over P$_4$O$_{10}$. Yield: 1.78 g (67%). *Anal.*: C, 49.85; H, 3.50; N, 11.82; Cl, 14.26. Calculated for [Ru(bipy)$_2$Cl$_2$]: C, 49.58; H, 3.33; N, 11.57; Cl, 14.64.

cis–trans-*Dichlorobisbipyridylruthenium(II)*

trans-[Ru(bipy)$_2$py$_2$](ClO$_4$)$_2$ [2] (0.40 g) was slurried with Dowex 1-X1 (50–100 mesh, Cl$^-$ form) until solution of the insoluble perchlorate was complete. After filtering from the resin the solution of the chloride salt was evaporated to dryness, dissolved in 15 ml water and 5 ml conc HCl and 3 ml ethanol added. After 40 min boiling the solution was cooled and the product washed with water after filtration, and dried *in vacuo* over P$_4$O$_{10}$. Yield: 0.21 g (84%).

Conversion of a sample to [Ru(bipy)$_2$py$_2$] (ClO$_4$)$_2$ showed both *cis*- and *trans*-isomers, in equal amounts.

Conversion of trans-*[Ru(bipy)$_2$py$_2$]$^{2+}$ to* cis-*isomer*

To determine if the repeated cycling through the *bis*-pyridine complex was necessary to achieve isomeric purity an experiment was performed by heating a solution of [Ru(bipy)$_2$py$_2$]$^{2+}$ (from [Ru(bipy)(py)$_4$]$^{2+}$ and bipy), removing aliquots periodically, and checking for isomeric composition (infrared). After 30 min on the steam bath more *trans* than *cis* is present. After 5½ hr the characteristic infrared peaks are nearly equal, indicating some small amount of conversion of *trans* to *cis*. However, this was not considered to be synthetically helpful.

Results and Discussion

A new synthesis of *cis*-Ru(bipy)$_2$Cl$_2$] and the *cis–trans* mixture is presented. Using this preparation we have been successful in reproducing, for example, the literature preparations of [Ru(bipy)$_2$(NO$_2$)$_2$] [3] and [Ru(bipy)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$ [4]. While our attempts at reproducing Dwyer's [Ru(bipy)$_2$Cl$_2$] give a material which does produce [Ru(bipy)$_2$py$_2$]$^{2+}$, this starting material fails to reproduce the above two complexes. Apparently other workers have encountered similar difficulty [5].

We have not been successful in isolating pure *trans*-[Ru(bipy)$_2$Cl$_2$]. However, the *cis–trans* mixture may be useful for giving separable *cis–trans* mixtures of other complexes. Unfortunately, the cleanest *cis–trans* mixture appears to be formed in the reaction starting with pure *trans*-[Ru(bipy)$_2$py$_2$](ClO$_4$)$_2$. This procedure is a bit more laborious.

If [Ru(bipy)$_2$Cl$_2$] is isolated from the [Ru(bipy)$_2$py$_2$]$^{2+}$ solution without going through the reconversion to [Ru(bipy)$_2$py$_2$]$^{2+}$ the product is contaminated by a residue. Dissolving crude [Ru(bipy)$_2$Cl$_2$] in hot water leaves a residue (*ca.* 30%) which analyses as a polymer (Ru$_3$(bipy)$_8$Cl$_8$). This residue will react with pyridine to produce [Ru(bipy)$_2$py$_2$]$^{2+}$ (primarily *cis*) and hence it does not detract from the overall yield in going through the recommended three cycles. But it could interfere in subsequent work if not removed.

Isomerization of *trans*-[Ru(bipy)$_2$Cl$_2$] appears to occur in the treatment with hydrochloric acid. If [Ru(bipy)$_2$py$_2$]$^{2+}$ is held on the steam bath for six hours very little isomerization occurs, while pure *trans*-[Ru(bipy)$_2$py$_2$]$^{2+}$ quickly gives the *cis–trans* mixture on heating with hydrochloric acid. This isomerization probably occurs through a protonated seven coordinate intermediate, the proton bonding to a filled t$_{2g}$ orbital.

In this work we have extensively utilized the characteristic difference in the infrared spectra of the *cis*- and *trans*-isomers of [Ru(bipy)$_2$py$_2$](ClO$_4$)$_2$ [2]. We have found this to be a useful analytical technique for establishing the presence of isomers or for determining structure in a few situations. In the *cis*-complex the pyridine ring mode appears at 706 cm^{-1}, while in the *trans* it appears at 698 cm^{-1}. As would be inferred from all previous work, the Dwyer preparation of [Ru(bipy)$_2$Cl$_2$] leads to [Ru(bipy)$_2$py$_2$](ClO$_4$)$_2$ which is exclusively *cis*.

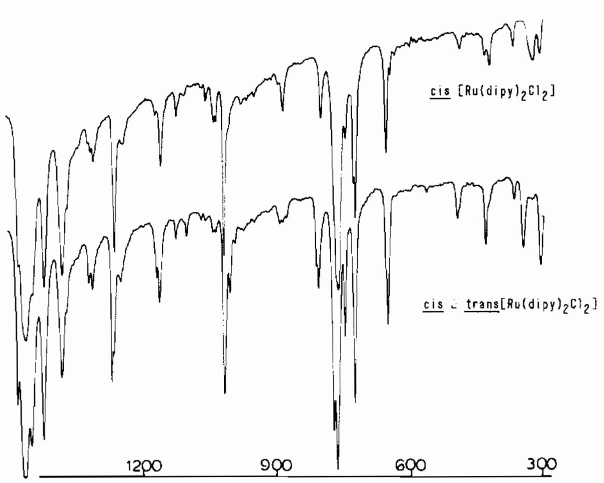

Figure.

The infrared spectra of *cis*-[Ru(bipy)$_2$Cl$_2$] and the *cis–trans* mixture are shown in the Figure. A few additional bands in the mixture we attribute to the *trans*-isomer. Perhaps the most important differences are: a) splitting of the 760 cm^{-1} band, *trans* at 767, *cis* at 759 with higher energy shoulders; b) splitting of the 800 cm^{-1} band, *trans* at 807, *cis* at 800; c) the *trans* appears to have a peak at 342 cm^{-1}, while the *cis* has one at 322.

One should be able to identify the *trans* isomer, or detect it in mixtures by means of the infrared spectrum.

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References

1 F. P. Dwyer, H. A. Goodwin and E. C. Gyarfas, *Aust. J. Chem., 16,* 544 (1963).
2 R. A. Krause, *Inorg. Chim. Acta, 22,* 209 (1977).
3 J. B. Godwin and T. J. Meyer, *Inorg. Chem., 10,* 471 (1971).
4 G. M. Brown, R. W. Callahan and T. J. Meyer, *Inorg. Chem., 14,* 1915 (1975).
5 M. Mukaida, M. Yoneda and T. Nomura, *Bull. Chem. Soc. Japan, 50,* 3053 (1977).