Inorganica Chimica Acta, 113 (1986) 161–162

An Improved Synthesis of Potassium Hexacyanoruthenate(II)

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Received August 22, 1985

Abstract

A new procedure for the synthesis of $K_4Ru(CN)_6$ is detailed. The synthesis involves bromine oxidation of an aqueous solution of ruthenium chloride, conversion of the perruthenate to ruthenate with base, and reaction of ruthenate with cyanide ion. Good yields (77%) of pure compound are obtained.

Introduction

Claus first reported $K_4Ru(CN)_6$ in 1854 [1] but Howe some years later studied the compound in more detail [2]. Howe observed that $RuCl_3$ boiled with concentrated aqueous potassium cyanide yielded the compound but in impure form; he commented that reaction of aqueous K_2RuO_4 heated with potassium cyanide might probably be the most satisfactory method of synthesis. This procedure requires the fusion of ruthenium metal or oxide with potassium hydroxide–potassium nitrate mixture. These two procedures have been those employed by most workers. One variation of the former procedure uses active carbon to facilitate the reaction between $Ru(OH)Cl_3$ and excess potassium cyanide [3].

We have devised a simple method for preparing $K_4Ru(CN)_6$ derived from Howe's early suggestion; the method is rapid, reproducible, uses readily available hydrated ruthenium trichloride, and leads to pure material.

Experimental

Reagents

Bromine water solution, 0.21 M Br_2. Add 3.4 g of bromide to 100 ml of water. The mixture is shaken and allowed to stand for several hours before use.

Procedure

To 40.0 ml of 0.21 M bromine water solution add 1.00 g of $RuCl_3 \cdot 3H_2O$. The flask is swirled gently for sixty seconds to completely dissolve the ruthenium trichloride. After sixty seconds immediately add 2.50 g of solid potassium hydroxide, mix and let stand for seven minutes giving a dark brown solution. Add 10.00 g of solid potassium cyanide, mix for 30 s, and then heat the resultant dark greenish brown solution. Boil; the solution becomes green, gradually lightens, and finally is just colorless, at which point the reaction is over (in 39 min). The colorless solution is immediately allowed to cool to room temperature. Add 60.0 ml of absolute methanol and filter the resulting precipitate. The product is washed with 1:1 methanol:water until the wash liquors are no longer basic (approximately 225 ml are required). The precipitate is then washed with 20 ml of absolute methanol followed by 20 ml of diethyl ether. A crude yield of 1.30 g is obtained.

The crude product is dissolved in 25 ml of water and 25 ml of methanol added. After one hour the precipitate is collected by filtration and washed successively with 25 ml of 1:1 methanol:water, 8 ml of methanol, and finally with 8 ml of diethyl ether. White felted crystals weighing a total of 1.22 g (77%) are obtained. *Anal.* (Baron Consulting Co., P.O. Box 663, Orange, Conn. 06477.) Calc. for $K_4RuC_6N_6$: C, 17.42; N, 20.32; H, 0. Found: C, 17.13; N, 20.03; H, none %.

Several steps in the above procedure require explanation. The time period stated before the addition of reagents must be observed, or the desired product will not be obtained. A small change in the concentration of any of the reagents also results in a different product being obtained. If the solution is left on the hot plate after it becomes colorless fine black particles are observed.

Physical Measurements

Infrared spectra were obtained in mineral oil mulls supported on CsI plates from 4000 to 200 cm^{-1} using a Perkin-Elmer 283. Visible spectra were obtained on aqueous solutions using a Cary 17D; absorbance values were read directly from the display meter at the wavelength maximum using an instrument time constant of 25 s. For cyclic voltammetry millimolar aqueous solutions, 0.10 M

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0020-1693/86/$3.50

in potassium nitrate were examined using a BAS CV 27 Voltammograph and a Houston Instrument 100 recorder. The standard three electrode configuration was employed with platinum working and counter electrodes and a Ag/AgCl reference electrode. As a standard, Fe(1,10-phenanthroline)$_3$-$(ClO_4)_2$ was used in the same medium; this compound has a potential of 1.06 V [4].

Results and Discussion

The procedure we have described appears to be the most convenient one yet reported. While crystallization from water yields the trihydrate methanol precipitation gives the anhydrous salt. Following the above directions gives a pure white solid; altering the conditions frequently yields lavender materials.

The infrared spectrum confirms the absence of water in the compound. Nakagawa and Shimanouchi [5] have performed a detailed analysis of the infrared spectrum of the trihydrate. Our anhydrous salt appears to show slightly better resolution in the cyanide stretching region but the major details are the same. We observe the Ru–CN stretch at 546 and the Ru–CN bend at 368 cm^{-1}, compared to their values of 550 and 376 cm^{-1}. These slight differences could be due to the calibration of our instrument.

Our compound gives an ultraviolet spectrum identical in appearance to that shown by Robin [6]. Our maximum appears at 205.5 nm with a molar extinction coefficient of $3.89 \pm 0.18 \times 10^4$ M^{-1} cm^{-1} (the average of three separate determinations), in agreement with the spectrum shown by Robin. Chastain and Mason [7] report an extinction coefficient at 205 nm of 43 500 M^{-1} cm^{-1}.

We can find no previous report of cyclic voltammetry on this compound; DeFord and Davison [8] obtained a formal potential polarographically of 0.97 V in 0.2 M KCl solution. We observe a value of 0.97 V (corrected to the hydrogen scale) in 0.10 M KNO_3 in good agreement with the polarographic value.

In this synthesis concentrations and timing have been found to be important for success. Consideration of a plausible pathway can suggest the necessity for this procedure. Howe [2] used $KRuO_4$ produced by alkali fusion; this is known to produce RuO_4^{2-} rapidly in hot aqueous alkali [9]. The result of bromine oxidation of $RuCl_3$ is known to be the perruthenate anion. Thus, at the time of addition of potassium cyanide in our synthesis both the green perruthenate and the orange ruthenate are present, giving a dark green–brown solution. During the course of the reaction the color becomes green, gradually lightening. We conclude from this that ruthenate, rather than perruthenate, is the species rapidly reacting with cyanide since its orange color never develops during the reaction.

In the present procedure heating must be discontinued as soon as the solution has become colorless, otherwise a dark byproduct begins to form. This is most likely a bridged oligomeric compound. The $Ru(CN)_6^{4-}$ anion is known to slowly decompose in solution and the hydrolysis product may then react to produce oligomers.

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