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SELENIUM ANALOGUES OF β-DIKETONES. I. SYNTHESIS OF 1,1,1-TRIFLUORO-4-(2-THIENYL)-4-SELENO-3-BUTEN-2-ONE (SeTTA) AND ITS ANALYTICAL APPLICATION

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The synthesis of a new chelating reagent, 1,1,1-trifluoro-4-(2-thienyl)-4-seleno-3-buten-2-one (SeTTA) by the reaction of hydrogen selenide in a stream of nitrogen gas with TTA in absolute ethanol in the presence of hydrogen chloride is described. The analytical application of SeTTA is also discussed.

Introduction

In recent years, 1,1,1-trifluoro-4-(2-thienyl)-4-mercapto-3-buten-2-one (abbreviated as STTA) in which one oxygen atom of TTA (Thenoyl-trifluoroacetone) is replaced with sulfur has been found to form stable and extractable chelates with a specific color,[1] and it has been used for several analytical purposes: on the spectrophotometric determination of Co(II),[2] the separation of Hg(II), Co(II), and Zn(II) by extraction chromatography,[3] the separation of Co(II), Ni(II), Cu(II), Zn(II), Hg(II), Pb(II), and Cd(II) by thin-layer chromatography,[4] the separation of Ni(II) and Co(II) by a back-extraction process,[5] and some aspects of the extraction behavior of STTA complexes and their adducts with TOPO.[6]

The present author has now synthesized a new chelating reagent, 1,1,1-trifluoro-4-(2-thienyl)-4-seleno-3-buten-2-one (abbreviated as SeTTA), in which one oxygen atom of TTA is replaced with selenium in anticipation of enhanced selectivity and sensitivity due to the altered donor atom, and investigated its reactivity with various metal ions from the point of view of analytical application.

Experimental

The SeTTA was synthesized by the reaction of hydrogen selenide in a stream of nitrogen gas with TTA in absolute ethanol in the presence of hydrogen chloride by the following procedure. The starting substance, TTA, was first dried in a desiccator containing silica gel. Anhydrous ethanol was prepared by adding 5 g of metallic sodium to 500 ml of commercial reagent-grade ethanol (99.5%), by heating it under reflux for 5 to 8 hr, and by then distilling the alcohol.

Hydrogen chloride gas was generated by dropping concentrated sulfuric acid onto solid sodium chloride of a suitable amount in a flask of an eggplant type under occasional heating; the gas was introduced from the outlet tube of the flask into a washing bottle containing concentrated sulfuric acid. Hydrogen selenide gas was prepared by the action of 2 M hydrochloric acid on aluminium selenide in a flask of an eggplant type under occasional heating and dried through a glass tube containing anhydrous calcium chloride, and thereafter passed into the reaction vessel. The dehydration of these three materials, ethanol, hydrogen chloride, and hydrogen selenide, could lead a worker to a successful synthesis of SeTTA.

The synthesis in this work was done by the following method. Into a 300 ml flask with three necks, 5 g of TTA and 100 ml of the dehydrated ethanol were put through the large central neck of the flask, and then the content of the vessel was cooled to 0 °C in an ice bath. The dried hydrogen chloride gas was introduced through the first slender neck into the vessel for about 30 minutes. The dried hydrogen selenide gas in a stream of nitrogen gas was then passed through the second slender neck into the reaction vessel for about 30 minutes under occasional shaking by hand. Here the nitrogen gas from a steel bomb was previously introduced into a washing bottle containing a potassium hydroxide solution of pyrogallol in order to exclude oxygen and dried through another one containing concentrated sulfuric acid. The large central neck was also useful for letting the gases out under slow suction.

The hydrogen selenide gas which has disagreeable odor causing irritation of eyes, nose, and throat, was finally collected by passing through it into a weak acid solution of zinc chloride. The content of the vessel began to turn into deep orange brown even after passing hydrogen selenide gas for only about 5 minutes, but the passing of the gas was continued for 30 minutes in order to complete the reaction. Some red brown product (selenium or unknown substances) was deposited on the inside wall or the bottom of the vessel. After filtering, the content was mixed with chloroform in a separating funnel and was washed with an appropriate amount of a dilute hydrochloric acid solution. The chloroform solution containing SeTTA was dried by using anhydrous sodium sulfate, and the product was recovered by evaporation of the solvent under low pressure. The SeTTA thus obtained was a red oil (yield 30-70%), but once it was placed in the air, it turned slowly into a red orange crystal, probably diselenide, a dimer of SeTTA, which showed a melting point of 55-60 °C. Although the solid product or its solution in chloroform was susceptible to atmospheric oxidation, the diselenide formed could be readily reduced with sodium sulfite solution. The solution of SeTTA in chloroform was considerably stable. The SeTTA and its solution in chloroform were sealed in a brown-colored bottle in a nitrogen atmosphere and stored in a refrigerator kept at 5 °C.

Results and Discussion

Although the reaction mechanism may probably be quite complex, the preference for substitution of oxygen by selenium on the carbonyl group adjacent to C_4H_3S and CF_3 appears to be $C_4H_3S > CF_3$ as in the synthesis of STTA.7) The NMR resonance (τ of TMS reference) of carbon tetrachloride solutions of TTA, STTA and SeTTA was 3.61, 3.08 and 3.52 on the chelate ring proton, and was -4.36, -3.90 and -0.20 on the proton resonance of enol, thio enol and seleno enol, respectively. The selenol proton shows a shift to a higher value, which is consistent with the lesser electronegativity of selenium as compared to oxygen or sulfur. The infrared spectral bands and their possible assignment (cm^{-1}, C=O) of TTA, STTA and SeTTA in nujol were 1604, 1620 and 1655, respectively. The visible and ultraviolet spectra of TTA, STTA and SeTTA are shown in Figure 1. The solution of SeTTA in chloroform (λ_{max}= 348.5 nm, orange brown) resembles that of STTA (λ_{max}= 366.0 nm, red) in possessing one strong absorption band in the visible region, displaced to somewhat shorter wavelength.

The visible spectrum of the diselenide in chloroform is similar to that of TTA.

The diselenide does not form extractable complexes with any cations, while the SeTTA (10^{-2} M) forms with many metals (trace - 10^{-1} M) strongly colored complexes that can be extracted into chloroform in the region of pH 1-7.

Each chelate showed its own specific color, had an absorption maxima (λ_{max} , nm): Fe(II), 338.5, 350-560 (shoulder), dark red; Co(II), 346.5, brown yellow; Ni(II), 346.5, yellow brown; Cu(II), 342.0, brown green; Zn(II), 344.5, yellow brown; Hg(II), 343.5, yellow; Pb(II), 348.0, dark brown; Cd(II), 348.5, yellow brown; Pd(II), 346.5, brown; Ag(I), 347.5, dark brown, and Au(III), 346.5, yellow brown. The molar absorption coefficient of the SeTTA and the representative iron chelate in chloroform were about 7600 and 20000 at 350 nm.

Thus the SeTTA may prove to be a good extraction-spectrophotometric reagent for these metal ions.

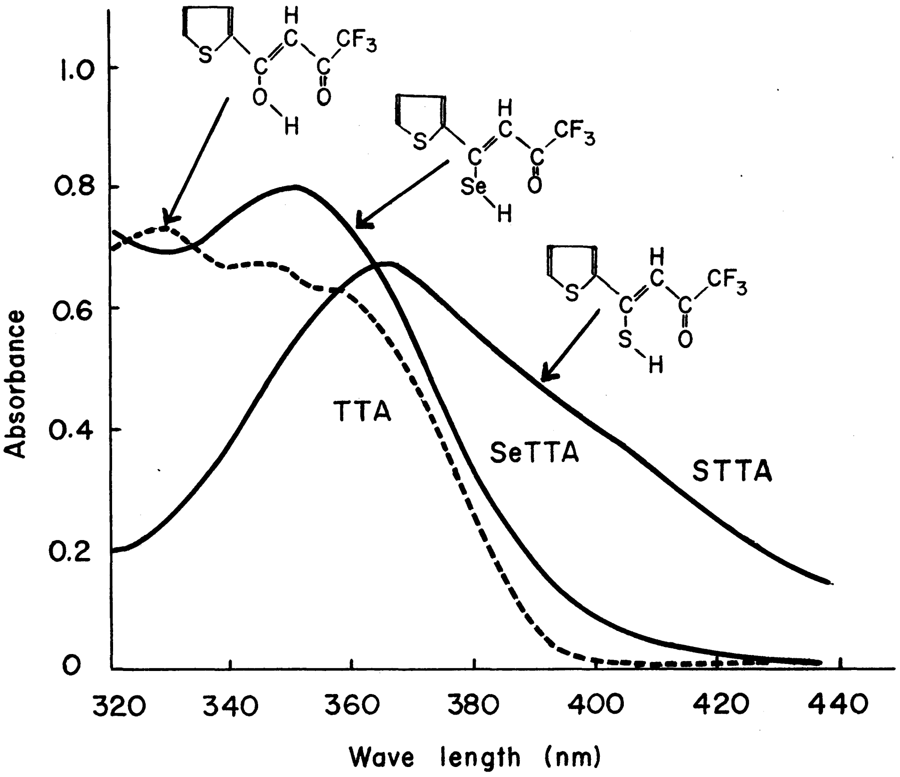

Figure 1. Electronic spectra of 6×10^{-5} M TTA, 4×10^{-5} M STTA and 10^{-4} M SeTTA in chloroform solution

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