A Rapid Synthetic Method for the Preparation of Two Tris-Cobalt(III) Compounds

Donald C. Jackman and D. Paul Rillema
University of North Carolina-Charlotte, Charlotte, NC 28223

A standard experiment used in inorganic laboratory courses is the synthesis of tris(ethylenediamine)cobalt (III) and the subsequent separation and study of the optical isomers of this material. The techniques for preparation of this compound are standard but suffer from the problem of requiring a 4-h sparge with air to oxidize the cobalt (III) complex to the desired cobalt (III) complex. We report here a method of preparation of tris(ethylenediamine)cobalt (III) and tris(2,2'-bipyridine)cobalt (III) that will shorten the preparation time by approximately 3 h.

Synthesis of Tris(ethylenediamine)cobalt(III) Ion

Fourteen grams (50 mmol) of CoSO₄·7H₂O was dissolved in 25 mL of H₂O. Twelve milliliters (10.8 g, 180 mmol) of anhydrous ethylenediamine (en) was dissolved in 25 mL of H₂O, reacted with 5 mL of concentrated (12 M) hydrochloric acid, and then cooled to room temperature in an ice bath. These two solutions were added, with stirring, to a 250-mL Schlenk-ware flask, and 2 g of activated charcoal was added to the resulting solution. The mixture was sparged (with stirring) with a rapid stream of CH₄ from a lecture bottle for 2 min during which time the reaction mixture became quite warm due to the exothermicity of the reaction. The excess CH₄ was removed from the solution by vacuum aspiration until frothing ceased. Then the solution was heated (~90 °C) to remove remaining CH₄ from the reaction mixture. The pH of the solution (still hot) was adjusted to about 7 with aqueous ethylenediamine, reheated, and suction filtered (Buchner funnel, Whatman #1 qualitative filter paper) to remove the charcoal from the reaction mixture. The hot filtrate was cooled in an ice bath, treated with saturated aqueous NH₄PF₆ dropwise, and an orange solid slowly formed. The orange solid was isolated with a 60-mL medium-frit Buchner funnel, washed once with 30 mL of cool water and three times each with 30-mL portions of room-temperature ethanol and room-temperature ethyl ether, and dried in a room-temperature vacuum oven. The yield of [Co(en)₂(PF₆)₂] was 12.8 g (58% yield). The time required for synthesis and isolation of the product was approximately 1 h.

The UV-visible spectrum of the product in aqueous solution showed peaks at 339 nm (ε = 119 M⁻¹ cm⁻¹) and 467 nm (ε = 138 M⁻¹ cm⁻¹). These values are consistent with the literature. Cyclic voltammetry in aqueous 0.1 M KNO₃ (Pt working electrode and Pt counter electrode) yielded an irreversible Co²⁺/³⁺ reduction wave at approximately +0.70 V versus SSCE (sodium saturated calomel electrode).

B-Synthesis of Tris(2,2'-bipyridine)cobalt(III) Ion

One-tenth of a gram (0.77 mmol) of anhydrous CoCl₃ was added to 0.5 g (2.7 mmol) of 2,2'-bipyridine (bpy) dissolved in 50 mL of 0.1 M HCl. The mixture was stirred in a 100-mL Schlenk-ware flask. To this solution was added 0.1 g of activated charcoal, and the resulting mixture was sparged, while stirring, with a rapid stream of CH₄ for 30 s. The excess CH₄ was removed from the solution as described above. The hot mixture was suction filtered (Buchner funnel, Whatman #1 qualitative filter paper) to remove the charcoal. The filtrate was cooled to room temperature and treated with saturated aqueous NH₄PF₆ dropwise, whereupon a yellow solid formed immediately. The product, tris(2,2'-bipyridine)cobalt (III) hexafluorophosphate, [Co(bpy)₃(PF₆)₆], was isolated on a medium-frit Buchner funnel and washed twice each with room temperature water, ethanol, and ethyl ether. The product yield was 0.59 g (71% yield). The total time required for preparation and isolation was about 50 min. The product was dried in a room-temperature vacuum oven.

The UV-visible spectrum of this compound dissolved in acetonitrile exhibited three peaks: 305 nm (ε = 4.34 × 10⁴ M⁻¹ cm⁻¹), 318 nm (ε = 3.69 × 10⁴ M⁻¹ cm⁻¹), and 455 nm (ε = 77.5 M⁻¹ cm⁻¹) and are in agreement with previously published results. Cyclic voltammetry (0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile as supporting electrolyte/solvent, Pt working and counter electrodes) gave reversible Co²⁺/³⁺, Co³⁺/⁴⁺, and Co⁴⁺/⁵⁺ waves at +0.31, −0.59, and −1.69 V versus SSCE, respectively.

Acknowledgment

We thank the Office of Energy Science of the Department of Energy under Grant DE-F605-84ER-13263 for support.

1 Author to whom correspondence should be addressed.
4 Ellis, P.; Wilkins, R. G.; Williams, M. J. G. J. Chem. Soc. 1957, 4456. This reference reported only the visible peak.