

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA, GEORGIA 30332**Optically Active Tris(1,10-phenanthroline) Complexes of Chromium(III) and Cobalt(III) by Resolution and Synthesis¹**

BY CHING S. LEE, E. M. GORTON, H. M. NEUMANN, AND HAROLD R. HUNT, JR.

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Preparation of the optical isomers of the tris(1,10-phenanthroline) complexes of Cr(III) and Co(III) is reported. Resolution of the Cr(III) complex and partial resolution of the Co(III) complex has been achieved by utilizing potassium antimonyl-*d*-tartrate as resolving agent in aqueous ethanol medium. In addition, the dextrorotatory isomers have been synthesized by a second-order asymmetric process.

Introduction

During recent years renewed interest has been shown in the preparation and properties of optically active coordination compounds.² A number of studies have been concerned with the octahedral complexes of 1,10-phenanthroline with transition metal ions, and resolution procedures have been reported for the tris complexes of iron(II),³ ruthenium(II),⁴ osmium(II),⁵ and nickel(II).⁶ By oxidation of the resolved complexes of divalent iron, ruthenium, and osmium, the optically active tris(1,10-phenanthroline) complexes of iron(III),³ ruthenium(III),⁴ and osmium(III)⁷ have been obtained. Until now there have been no reports of the direct resolution of a trivalent ion, although an unsuccessful attempt to resolve Co(phen)₃³⁺ has been reported.⁸

This work was undertaken in order to obtain the optical isomers of 1,10-phenanthroline complexes of Co(III) and Cr(III) for use in electron-transfer studies. In this paper we report the resolution of Cr(phen)₃³⁺ and Co(phen)₃³⁺, together with a method for synthesizing the dextrorotatory isomers of these complexes by a second-order asymmetric process.

Experimental Section

Materials.—1,10-Phenanthroline monohydrate (Matheson Coleman and Bell) was used without further purification. Potassium antimonyl-*d*-tartrate was recrystallized from water. Silver antimonyl-*d*-tartrate was prepared from silver nitrate and potassium antimonyl-*d*-tartrate by metathesis in aqueous solution. Tris(1,10-phenanthroline)cobalt(III) perchlorate was prepared by known methods.⁹

Chromium(II) sulfate pentahydrate was prepared either by dissolving pure chromium metal in dilute sulfuric acid¹⁰ or by reducing an acidic solution of Cr₂(SO₄)₃·*n*H₂O in a Jones reductor, adding the resulting Cr(II) solution to cold, concentrated sul-

furic acid, and collecting the CrSO₄·5H₂O product on a sintered-glass filter

Both preparations were conducted in a three-neck flask containing a gas inlet and outlet at one neck, a Jones reductor or serum stopper at the central neck, and at the third neck a filter device following the design of Ocone and Block.¹¹ An inert atmosphere was provided by a flow of nitrogen gas which had been purified by scrubbing successively with solutions of alkaline pyrogallol and chromium(II) sulfate. The product was washed with cold water and ethyl alcohol and was dried under vacuum. The product contained traces of CrSO₄·H₂O (white) and chromic salts in addition to the blue CrSO₄·5H₂O. The Cr(II) content was determined by potentiometric titration with a standard K₂Cr₂O₇ solution. *Anal.* Calcd for CrSO₄·5H₂O: Cr, 21.8. Found: Cr, 22.0.

Since the salt slowly dehydrates on standing in a vacuum desiccator, the Cr(II) content was redetermined prior to each use.

Tris(1,10-phenanthroline)chromium(III) perchlorate was prepared as described by Herzog,¹² except that chromium(II) sulfate pentahydrate rather than chromium(II) iodide was used as the starting material. *Anal.* Calcd for Cr(phen)₃(ClO₄)₃·2H₂O: C, 46.7; H, 2.62; N, 9.09. Found: C, 46.8; H, 2.63; N, 9.06.

Measurements.—Spectra of the tris(1,10-phenanthroline) complexes of chromium(III) and cobalt(III) were measured at various concentrations over the wavelength range 200–700 mμ, using a Cary Model 14 recording spectrophotometer. Both spectra show the intense ultraviolet absorption bands characteristic of 1,10-phenanthroline. The spectrum of the Co(III) shows in addition a small shoulder on the tail of the large ultraviolet absorption in the region 450–550 mμ. This shoulder was resolved by an empirical method,¹³ indicating an absorption maximum at 470 mμ, with a molar extinction coefficient of 42 M⁻¹ cm⁻¹. The spectrum of the chromium complex shows a shoulder in the region 400–460 mμ. This was resolved by the same procedure, indicating an absorption maximum at 426 mμ, with a molar extinction coefficient of 384 M⁻¹ cm⁻¹.

The optical activity of the various samples was determined with a Bellingham and Stanley polarimeter and a sodium lamp, with cells of either 1- or 2-dm length. In expressing the concentration of these solutions, the symbol % means grams of solute per 100 ml of water.

Optical rotatory dispersion curves were determined for the resolved complexes using a Perkin-Elmer ORD attachment in conjunction with a Cary Model 14 recording spectrophotometer. These are shown in Figure 1.

Resolution of Tris(1,10-phenanthroline)chromium(III) Perchlorate Dihydrate.—Moist Dowex 1-X8 ion-exchange resin in the chloride form was added in small increments to a suspension

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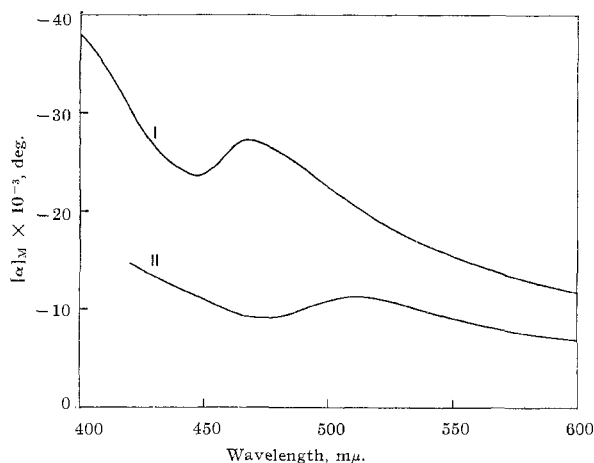


Figure 1.—Optical rotatory dispersions of (I) l -Cr(phen) $_3$ (ClO $_4$) $_3$ ·2H $_2$ O and (II) l -Co(phen) $_3$ (ClO $_4$) $_3$ ·2H $_2$ O. The molecular rotation $[\alpha]_M$ is related to the specific rotation $[\alpha]$ by $[\alpha]_M = (MW/100)[\alpha]$.

of 2.03 g of tris(1,10-phenanthroline)chromium(III) perchlorate dihydrate (2.20×10^{-3} mole) in 25 ml of water, converting the complex to the highly soluble chloride salt. When the complex was all in solution, the resin was filtered off. Silver antimonyl- d -tartrate (2.66 g, 6.60×10^{-3} mole) was added to the solution with stirring, and after several minutes the resulting silver chloride was filtered off. The solution of tris(1,10-phenanthroline)chromium(III) antimonyl- d -tartrate was warmed to about 50°, and absolute ethanol was slowly added until the solution became slightly cloudy. Cooling the solution to ice-water temperature yielded the yellow crystalline diastereoisomer, which was collected on a sintered-glass filter, washed with cold, absolute ethanol and with ether, and air dried. The yield was 1.23 g. The filtrate was heated to about 40°, and again absolute ethanol was added to the point of incipient precipitation. On cooling, a precipitate formed which was isolated as before. This second fraction weighed 0.93 g. In a similar manner, a third fraction (0.82 g) and a fourth fraction (0.072 g) were obtained. Optical rotations of the diastereoisomers were measured using 10.0 mg of complex per 5 ml of solution. The respective rotations of fractions one through four were observed to be -0.89 , $+1.36$, $+0.96$, and $+0.40^\circ$. Fraction one was further purified by dissolving the solid in 25 ml of water, warming to about 40°, and adding alcohol to precipitate the least soluble fraction. This process of fractional crystallization was continued until there was no further change in the optical rotation of a 0.20% solution of the diastereoisomer in water. The maximum rotation observed for 10.0 mg of the complex in 5 ml of water was -1.41° . The complex was then dissolved in water, and sodium perchlorate was added to precipitate the pure l -tris(1,10-phenanthroline)chromium(III) perchlorate dihydrate. The precipitate was filtered, washed with small quantities of water, alcohol, and ether, and then dried under vacuum. The specific rotation, calculated from measurements on a 0.200% solution, was -1320° (g/cc) $^{-1}$ dm $^{-1}$.

Because of its high solubility in the water-ethanol mixture, pure d -tris(1,10-phenanthroline)chromium(III) antimonyl- d -tartrate could not be obtained by fractional crystallization. A procedure for isolation of the d complex follows. After precipitating the less soluble l -tris(1,10-phenanthroline)chromium(III) antimonyl- d -tartrate, the filtrate is cooled in ice water and a solution of sodium perchlorate is added dropwise to the point of incipient precipitation. Sufficient sodium perchlorate to precipitate about one-half of the remaining complex is then added, and the resulting precipitate is filtered off. Excess sodium perchlorate is then added to the filtrate, precipitating pure d -tris(1,10-phenanthroline)chromium(III) perchlorate dihydrate. The specific rotation, calculated from measurements on a 0.200% solution, was $+1320^\circ$ (g/cc) $^{-1}$ dm $^{-1}$.

Partial Resolution of Tris(1,10-phenanthroline)cobalt(III) Perchlorate Dihydrate.—Five grams of Dowex 1-X8 ion-exchange resin in the chloride form was added with stirring to a suspension of 3.00 g of tris(1,10-phenanthroline)cobalt(III) perchlorate dihydrate in 60 ml of water at a temperature of about 60°. This procedure converted the difficultly soluble perchlorate salt to the more soluble chloride salt. The resin was removed by filtration and washed with several portions of water.

Silver antimonyl- d -tartrate (4.00 g) was added to the filtrate, whose volume was now 100 ml, resulting in the formation of silver chloride. The silver chloride was removed, and the solution was heated to 55°. Ethanol was then added slowly until cloudiness occurred; the volume of solution was now 520 ml and the temperature was 40°. The solution was cooled to room temperature and then filtered. The precipitate was washed with ethanol and dried by pulling air through the filter. The filtrate was saved for further treatment as described later. The precipitate (2.44 g) was dissolved in 60 ml of water and filtered to remove insoluble material. Ethanol was again used to precipitate part of the dissolved salt. A fraction, weighing 1.33 g, was isolated as before. The specific rotation of a 0.230% solution was -369° (g/cc) $^{-1}$ dm $^{-1}$. This fraction was again dissolved and treated with ethanol to produce a third fraction, weighing 1.11 g. The specific rotation of a 0.203% solution was -383° (g/cc) $^{-1}$ dm $^{-1}$.

The diastereoisomer was dissolved in 100 ml of water, and an excess of sodium perchlorate was added to precipitate l -tris(1,10-phenanthroline)cobalt(III) perchlorate dihydrate. The compound was collected on a sintered-glass filter, washed with water and alcohol, and then dried in air. The yield was 0.50 g. The specific rotation, calculated from measurements on a 0.200% solution, was -765° (g/cc) $^{-1}$ dm $^{-1}$.

An attempt was made to recover pure d -tris(1,10-phenanthroline)cobalt(III) perchlorate from the filtrate remaining from the first fractionation, using controlled addition of sodium perchlorate as in the case of the chromium complex. Two fractions, weighing 0.29 and 0.092 g, respectively, were obtained. The specific rotation of the latter, calculated from measurements on a 0.092% solution, was $+174^\circ$ (g/cc) $^{-1}$ dm $^{-1}$.

Synthesis of d -Tris(1,10-phenanthroline)chromium(III) Perchlorate.—A portion of hydrated chromous sulfate containing 1.7×10^{-3} mole of Cr(II) was added to a dry three-neck flask equipped with a gas inlet-outlet device, a serum stopper, and a sintered-glass filter device. After displacing the air in the flask with purified nitrogen, 10 ml of water was added with a hypodermic syringe to dissolve the chromium(II) sulfate, followed by 2.0 g of 1,10-phenanthroline (1.0×10^{-2} mole) dissolved in 20 ml of anhydrous ethyl alcohol. Potassium antimonyl- d -tartrate (2.27 g, 6.8×10^{-3} mole) dissolved in 20 ml of warm water was then added, and a yellow-green precipitate formed. The precipitate was collected on the filter, washed successively with degassed water and ethyl alcohol, and then dispersed in 50 ml of anhydrous ethyl alcohol. Iodine (0.60 g, 4.7×10^{-3} g-atom) dissolved in 30 ml of ethyl alcohol was then added as rapidly as possible, while a magnetic stirrer was used to stir the mixture. After several minutes, the alcohol was filtered off, leaving a brown solid. The solid was treated with 200 ml of water and filtered to remove insoluble residue. Addition of excess sodium perchlorate to the clear solution precipitated the complex perchlorate. The golden yellow crystals were filtered and washed with ice-cold water, alcohol, and ether. The product was recrystallized from water and dried in a vacuum desiccator. The yield of d -tris(1,10-phenanthroline)chromium(III) perchlorate was 1.25 g (80% of theoretical). The specific rotation, calculated from measurements on a 0.206% solution, was $+1320^\circ$ (g/cc) $^{-1}$ dm $^{-1}$.

Synthesis of d -Tris(1,10-phenanthroline)cobalt(III) Perchlorate.—A 0.5021-g sample of 1,10-phenanthroline monohydrate (2.53×10^{-3} mole) was dissolved in 50 ml of water heated to about 80°. To this was added 0.1179 g (0.495×10^{-3} mole) of cobalt(II) chloride hexahydrate in 5 ml of water. To the solution, still at 80°, was added 5 ml of a hot solution containing

1.0040 g (3.01×10^{-3} mole) of potassium antimonyl-*d*-tartrate. The solution was allowed to come to room temperature by standing in air and then chilled in an ice bath. An essentially quantitative precipitation of the cobalt(II) complex results. The precipitate was collected on a sintered-glass funnel. The solid was then added to 25 ml of water which had been previously chilled to 8° and saturated with chlorine gas. Chlorine gas was passed into the agitated suspension for 5 min. The suspension was then allowed to warm to room temperature, 10 ml of water was added, chlorine was passed into the system for 1 min, and the mixture was heated to 60°. The small amount of residue remaining at this time was filtered off. The perchlorate salt of the complex was precipitated by addition of 5 ml of a solution of sodium perchlorate and chilling in an ice bath. The yield of tris(1,10-phenanthroline)cobalt(III) perchlorate dihydrate was 0.4405 g (95.5% of theoretical). The specific rotation, calculated from measurements on a 0.100% solution, was $+796^\circ$ (g/cc) $^{-1}$ dm $^{-1}$.

Discussion

The data clearly indicate that the resolution of tris(1,10-phenanthroline) complexes of trivalent ions into their optical isomers has been achieved for the first time.

The complexes of Co(III) and Cr(III) both show anomalous rotatory dispersions (Figure 1), which are consistent with the absorption bands at 470 and 426 μ , respectively.

The preparation of Cr(phen)_3^{3+} from the chromium(II) complex has been found to be very sensitive to the mode of oxidation. Thus, dropwise addition of iodine in ethanol to the chromium(II) complex results in little or none of the tris(1,10-phenanthroline)chromium(III) complex, whereas *rapid* addition of iodine in

excess leads to a good yield of this complex. Other oxidizing agents (bromine, chlorine, potassium dichromate, and 30% hydrogen peroxide) behave similarly, but tend to give lower yields. The product of slow oxidation is a pink salt having a phenanthroline:chromium ratio of less than 3:1. Although it has not been fully characterized, it appears to be a bis(1,10-phenanthroline) complex of chromium(III). A probable explanation for these observations is that, during slow oxidation, $\text{Cr(phen)}_2(\text{OH})_2^{2+}$ catalyzes the hydrolysis of Cr(phen)_3^{3+} by means of a rapid electron-transfer reaction. A similar mechanism has been proposed for the hydrolysis of the tris(bipyridyl)chromium(III) ion.¹⁴

The syntheses of *d*- Cr(phen)_3^{3+} and *d*- Co(phen)_3^{3+} have some similarities to Dwyer's preparations of active trivalent complexes.^{3,4,7} The racemic complex Fe(phen)_3^{2+} , on standing in solution with the antimonyl-*d*-tartrate ion, eventually precipitates completely as the levorotatory isomer.³ Similarly, the high yields of the active Cr(III) and Co(III) complexes require that the Cr(II) and Co(II) complexes precipitate completely in only one of the diastereoisomeric forms with antimonyl-*d*-tartrate.

The great lability of the Cr(II) and Co(II) species requires oxidation of a suspension, rather than a solution, for obtaining a product of high optical purity. The synthetic procedures reported are ones which, of several modifications attempted, were most successful in this respect.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF IOWA, IOWA CITY, IOWA

Metal-Olefin Compounds. VIII. The Crystal Structure of a Norbornadiene-Silver Nitrate Complex, $\text{C}_7\text{H}_8 \cdot 2\text{AgNO}_3$

By N. C. BAENZIGER, H. L. HAIGHT, R. ALEXANDER, AND J. R. DOYLE

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The structure of $\text{C}_7\text{H}_8 \cdot 2\text{AgNO}_3$ was determined by single-crystal X-ray diffraction methods. The silver atoms are connected in chains by $\cdots\text{O}-\text{N}-\text{O}\cdots$ links of the nitrate groups. One double bond of the olefin forms the third ligand about the silver atom; the axis of the double bond lies approximately in the plane of the $\text{O}\cdots\text{Ag}\cdots\text{O}$ link of the chain so that the coordination about Ag is triangular-planar. Both double bonds of the olefin are coordinated to Ag atoms, so that the olefin forms a cross-link between two $\text{Ag}-\text{NO}_3$ chains.

Introduction

The crystal structures of several complexes of olefins with silver salts have already been reported—cyclooctatetraene-silver nitrate¹ and cyclooctatetraene dimer-silver nitrate.² In the preparation of complexes of norbornadiene (NBD) with metal salts, two

different complexes with AgNO_3 have been reported, $\text{NBD} \cdot \text{AgNO}_3$ ^{3,4} and $\text{NBD} \cdot 2\text{AgNO}_3$.³⁻⁵ The complex $\text{NBD} \cdot 2\text{AgNO}_3$ is most easily isolated, and its structure

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