hydrate was also observed for a washed sample of the pentahydrate that had been exposed for 3 months to an atmosphere with 20–40% relative humidity. In all cases, however, the weight loss corresponding to complete conversion of the penta- to the monohydrate was achieved only by heating the sample ultimately to about 200° for 1 hr.

The solid phases produced either by isothermal dehydration or by heating to 200° gave identical X-ray diffraction patterns, which were different from those of either the pentahydrate or the anhydrous salt. The *d* values and relative intensities of this new pattern are also listed in Table IV. A sample of the pentahydrate that had been dehydrated at room temperature almost to the monohydrate level slowly regained about 40% of its total weight loss when exposed to 100% relative humidity at room temperature for 19 days. The X-ray diffraction pattern of this partially rehydrated material was the same as that of the monohydrate. A similar observation was made by Panzer[27] in his study of the dehydration of calcium acetate monohydrate (10.3% H_2O) to the half-hydrate (5.4% H_2O). Even when the sample contained 9.2% H_2O, the X-ray diffraction pattern was solely that of the half-hydrate and showed no evidence for a mixture of the mono- and half-hydrates.

The shape of the thermogram in Fig. 2 suggests that the monohydrate was undergoing slow dehydration even below 250°. This was confirmed by holding a sample of the monohydrate at 225° for 17 hr., during which time it lost two-thirds of its water. Complete dehydration could be achieved in 24 hr. at 250°, but the anhydrous $Na_2WO_4 \cdot WO_3$ thus formed gave a clear, sharp X-ray powder diffraction pattern different from that for the anhydrous salt formed either by dehydration at 450°, at 700°, or by fusion of an equimolar mixture of anhydrous Na_2WO_4 and WO_3. The pattern for this low temperature modification is also given in Table IV. The X-ray evidence suggests that this phase transition, between 250 and 450°, is different from the one reported by Hoermann[6] at 550° for $Na_2WO_4 \cdot WO_3$.

The difference in thermal stability between the penta- and monohydrate is also reflected in the results obtained by Karl Fischer titrations. Under conditions that result in complete titration of all of the water in a crystalline hydrate like disodium tartrate dihydrate, only 75% of the total water present in $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$ reacted with the Karl Fischer reagent, indicating titration of 94% of the labile water. The monohydrate behaved like an anhydrous salt toward the titrant.

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[27] J. Panzer, *J. Chem. Eng. Data*, **7**, 140 (1962).

CONTRIBUTION FROM THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN,
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The Stereochemistry of Complex Inorganic Compounds. XXVII. Asymmetric Syntheses of Tris(bipyridine) Complexes of Ruthenium(II) and Osmium(II)

BY CHUI FAN LIU, NORA C. LIU, AND JOHN C. BAILAR, JR.

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It has been shown that asymmetric syntheses of the tris(bipyridine)ruthenium(II) ion, the tris(*o*-phenanthroline)ruthenium(II) ion, and tris(bipyridine)osmium(II) ion can be carried out simply. The ruthenium compounds can be obtained to contain as high as 63% of the levo isomer while the osmium compound can be prepared to contain 70% of the levo isomer.

The tris(bipyridine)ruthenium(II) complex was first prepared by Burstall[1] by fusing ruthenium(III) chloride with bipyridine at 250°. A more convenient method of preparation consists in refluxing an aqueous alcoholic mixture of potassium pentachlorohydroxoruthenate(IV), bipyridine, and sodium hypophosphite.[2] Since the tris(bipyridine)ruthenium(II) is octahedral, it is capable of existing in *d* and *l* forms. The resolution of this compound was carried out by Burstall.[1] The tris(bipyridine)osmium(II) complex was prepared in approximately the same manner using hexachloroosmate(IV) as starting material.[3] Unlike the ruthenium compound, however, the osmium derivative was not obtainable from aqueous solution. The resolution of the tris(bipyridine)osmium(II) ion into its optical antipodes was achieved by Burstall and coworkers.[3]

The present study deals with the asymmetric syntheses of tris(bipyridine) complexes of both ruthenium

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[1] F. H. Burstall, *J. Chem. Soc.*, 173 (1936).

[2] F. P. Dwyer, J. E. Humpoletz, and R. S. Nyholm, *J. Proc. Roy. Soc. N. S. Wales*, **80**, 212 (1946); F. P. Dwyer, *ibid.*, **83**, 134 (1949).

[3] F. H. Burstall, F. P. Dwyer, and E. C. Gyarfas, *J. Chem. Soc.*, 953 (1950).

and osmium. Several cases of asymmetric syntheses of cobalt(III) complexes have been reported in the literature[4] together with a case involving a copper(II) complex.[5] However, there has been no report of any other metal ion complexes being asymmetrically synthesized.

Experimental

Asymmetric Syntheses of Ruthenium(II) Compounds. (A) Syntheses in the Presence of *d*-Tartrate Ions.—The following is a representative procedure. Potassium aquopentachlororuthenate(III) (0.25 g.) was heated on a steam bath with 0.62 g. of sodium *d*-tartrate dihydrate in 15 ml. of water for 10 min. During this period the solution changed from its original red color to green, then to a stable red-brown. To this red-brown solution was added 0.30 g. of bipyridine and the mixture was heated for 2 hr. more on a steam bath. On addition of 2 ml. of 10% perchloric acid the desired compound crystallized out. It was filtered, washed with ice-cold 10% perchloric acid, then with ether, and air dried. *Anal.* Calcd. for $[Ru(C_{10}H_8N_2)_3](ClO_4)_2$: C, 46.81; H, 3.15; N, 10.92. Found: C, 46.65, 46.44; H, 3.16, 3.25; N, 11.07, 11.22. The yield of the complex was 66% of theoretical. An aqueous solution containing 0.0576 g. of complex per 100 ml. of solution gave an observed rotation of −0.134° at the D-line of sodium. The specific rotation was, therefore, −233°.

In one run, the tris(bipyridine)ruthenium(II) ion was isolated as the iodide through the addition of potassium iodide instead of perchloric acid. *Anal.* Calcd. for $[Ru(C_{10}H_8N_2)_3]I_2 \cdot 5H_2O$: C, 39.42; H, 3.72; N, 9.19. Found: C, 39.10; H, 3.50; N, 9.07. This iodide gave a specific rotation of −120° at the D-line of sodium.

The tris(*o*-phenanthroline)ruthenium(II) perchlorate was asymmetrically synthesized in the same manner to give a 72% yield of the product. *Anal.* Calcd. for $[Ru(C_{12}H_8N_2)_3](ClO_4)_2 \cdot 2H_2O$: C, 49.26; H, 3.22; N, 9.58. Found: C, 49.81; H, 2.98; N, 9.87. This product gave a specific rotation of −258° at the sodium D-line.

In the asymmetric synthesis of the tris(bipyridine)ruthenium(II) ion the experimental conditions could be varied to some extent. Increased heating time before the addition of bipyridine resulted in an increase in the total yield. An increased molar ratio of sodium *d*-tartrate to potassium aquopentachlororuthenate(III) also increased the total yield. A case in which the molar ratio of tartrate to ruthenate(III) was 6:1 and the heating time was 5 hr. resulted in a total yield of 88% and a yield of the levo isomer of 53% (based on the theoretical yield of 50% levo isomer in a nonstereospecific synthesis).

(B) Syntheses in the Presence of Sucrose.—Potassium aquopentachlororuthenate(III) (0.38 g.) and 2.0 g. of sucrose were heated on a steam bath in about 30 ml. of water for 5 hr. and 0.50 g. of bipyridine was added. After heating for 3 hr. more a few drops of concentrated perchloric acid were added. The crystallized tris(bipyridine)ruthenium(II) perchlorate was filtered, washed with ice-cold 10% perchloric acid, then with ether, and air dried. The compound was identified by its infrared spectrum. This product gave a specific rotation of −92° at the sodium D-line.

The product was also isolated as the iodide which gave a specific rotation of −70° at the D-line of sodium.

Asymmetric Syntheses of the Tris(bipyridine)osmium(II) Ion. (A) Synthesis from Ammonium Hexabromoosmate(IV).—A mixture of 0.71 g. of ammonium hexabromoosmate(IV), 1.4 g. of sodium *d*-tartrate, and about 30 ml. of water was heated on a steam bath for 8 hr., and 0.50 g. of bipyridine was added. After heating on the steam bath for 6 hr. more, a few drops of concentrated perchloric acid were added. The desired tris(bipyridine)osmium(II) perchlorate crystallized. The crystals were filtered, washed with ice-cold 10% perchloric acid, then with ether, and air dried. The compound was identified qualitatively by its infrared spectrum. The purity of the sample was determined by obtaining the visible absorption spectrum and comparing it with the spectrum of a standard sample prepared by the method of Burstall and co-workers.[3] It was found that the spectrum of the sample corresponded quantitatively to that of the standard. The product obtained in the synthesis gave a specific rotation of −1200° at λ 5461 Å. (The observed rotation of a 0.004% solution was −0.049°.)

(B) Synthesis from Osmium Tetraoxide.—A 1-g. ampoule of osmium tetraoxide was broken into a solution of 5.5 g. of sodium *d*-tartrate in about 50 ml. of water in a 125-ml. erlenmeyer flask. The flask was stoppered with a one-hole stopper equipped with a tube leading into a trap containing a solution of ferrous ammonium sulfate. The reaction mixture was heated on a steam bath for 3 days. Bipyridine was added and the mixture was heated for an additional 2–3 hr. The solution was filtered and potassium iodide was added. The desired tris(bipyridine)osmium(II) iodide crystallized. The crystals were filtered off, washed with distilled water, and air dried. The infrared spectrum of the product was identical with that of tris(bipyridine)osmium(II) iodide prepared by the method of Burstall and co-workers.[3] The visible spectrum of a 5.5×10^{-5} *M* solution of the product corresponded quantitatively to the spectrum given by the same authors. A 0.004% solution of this product gave an observed rotation of −0.035° at λ 5461 Å. The specific rotation was calculated to be −875°.

Discussion

Experimental results have shown that stereospecific syntheses of the tris(bipyridine)ruthenium(II) ion, the tris(*o*-phenanthroline)ruthenium(II) ion, and the tris(bipyridine)osmium(II) ion can be carried out rather simply. The specific rotation of the optically pure *l*-tris(bipyridine)ruthenium(II) perchlorate was determined to be −897° at the D-line of sodium. The specific rotation of −233° for the product obtained in the present investigation corresponds to the composition of 63% levo isomer and 37% dextro isomer. The fact that in some runs more than 50% yield of the levo isomer was obtained indicated that an asymmetric synthesis was accomplished.

In the synthesis the tartrate ion and the sucrose molecule apparently served both to direct the stereochemistry of the reaction and to reduce the central ion. In this connection it might be pointed out that the present synthesis gave higher yields of the tris(bipyridine)ruthenium(II) compounds than the method used by Dwyer and co-workers[2] where sodium hypophosphite was used as the reducing agent. In case of the tris(bipyridine)osmium(II) compounds the present investigation represents the first successful preparation of the compound in aqueous solution. The fact that osmium tetraoxide can be used directly in the synthesis is also of interest.

The optically pure tris(bipyridine)osmium(II) iodide was reported to have a specific rotation of −2200° at λ 5461 Å. The specific rotation of −875° observed for the product of the present synthesis corresponds to the composition of 70% levo isomer and 30% dextro

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[4] F. B. Jonassen, J. C. Bailar, and E. H. Huffman, *J. Am. Chem. Soc.*, **70**, 756 (1948).

[5] B. DasSarma and J. C. Bailar, *ibid.*, **77**, 5480 (1955).

isomer. The tris(bipyridine)osmium(II) perchlorate obtained in this investigation showed a specific rotation of −1200° as compared to −3300° reported for the optically pure substance.

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A Kinetic Study of Substitution Reactions of Some Gold(III) Complexes

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Rate constants for the reactions of $[Au(dien)Cl]^{2+}$ (dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$) and/or its conjugate base, $[Au(dien\text{-}H)Cl]^+$ (dien-H = dien less a proton), with the reagents Br^-, I^-, SCN^-, N_3^-, and OH^- are reported. The results reported for the Au(III) systems are compared with data available for analogous Pt(II) complexes.

Introduction

Kinetic studies of substitution reactions of square-planar complexes are largely limited to the chemistry of platinum(II).[1] Other low-spin d^8 systems such as complexes of Pd(II), Ni(II), Au(III), Rh(I), and Ir(I) are also known to be square-planar. Investigations on these systems have not yet been extensive.

Analogous four-coordinated Au(III) and Pt(II) complexes are isoelectronic and isostructural. It is therefore of interest to compare the rates and mechanisms of substitution reactions of Au(III) with similar Pt(II) complexes. Rich and Taube[2] have investigated the exchange of chloride ion with $AuCl_4^-$. No other detailed study has been reported on exchange or substitution reactions of Au(III) complexes. This is in part because only a rather limited number of Au(III) complexes have been prepared and characterized and because of the ease with which these systems are reduced to Au(I) and Au.

The preparation and aqueous solution chemistry of complexes of the type $[Au(dien)X]^{2+}$ and $[Au(dien\text{-}H)X]^+$ was recently reported.[3] This paper reports the results of a kinetic investigation on the reactions of $[Au(dien)Cl]^{2+}$ and/or $[Au(dien\text{-}H)Cl]^+$ with the reagents Br^-, I^-, SCN^-, N_3^-, and OH^-.

Experimental

(A) **Preparation of Materials.**—The preparation, aqueous solution chemistry, and ultraviolet spectrum of the $[Au(dien)Cl]Cl_2$ used in this study were reported earlier.[3]

(B) **Kinetic Studies.**—Solutions of $[Au(dien)Cl]Cl_2$ were prepared by dissolving a weighed amount of the complex in distilled water and adding a few milliliters of 0.3 *M* $HClO_4$ until the pH was *ca.* 2.0–2.5. The addition of acid ensured that none of the conjugate base was present in the solution. Under these conditions, hydrolysis of the complex did not occur, as judged from the same ultraviolet spectrum with and without added chloride ion. Therefore, the kinetics investigated were for reaction 1.

$$[Au(dien)Cl]^{2+} + Y^- \longrightarrow [Au(dien)Y]^{2+} + Cl^- \quad (1)$$

Reactions of the conjugate base with various reagents were carried out by mixing an aqueous solution of $[Au(dien)Cl]^{2+}$ with a phosphate buffer of pH 7, which contained the desired reagent. Thus, at this pH, the Au(III) complex was converted instantaneously to the conjugate base (2). The reaction studied

$$[Au(dien)Cl]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Au(dien\text{-}H)Cl]^+ + H_2O \quad (2)$$

then was that of the conjugate base with the added reagent (3).

$$[Au(dien\text{-}H)Cl]^+ + Y^- \longrightarrow [Au(dien\text{-}H)Y]^+ + Cl^- \quad (3)$$

Several kinetic runs were also carried out by allowing bromide ion to react with a solution of $[Au(dien\text{-}H)Cl]^+$ prepared from $[Au(dien)Cl]^{2+}$ and 1 equiv. of NaOH solution. The results were the same, within experimental error, as those obtained by allowing an aqueous solution of $[Au(dien)Cl]^{2+}$ to react with a phosphate buffer solution of pH 7 containing bromide ion. Thus, the buffer components do not affect the rate.

Kinetics of reaction 4 were studied by dissolving a weighed

$$[Au(dien)OH]^{2+} + Y^- + H^+ \longrightarrow [Au(dien)Y]^{2+} + H_2O \quad (4)$$

amount of $[Au(dien)X]^{2+}$ ($X^- = Cl^-, Br^-$) in water and adding 2 equiv. of NaOH solution, thereby producing $[Au(dien\text{-}H)OH]^+$ in solution. This solution was then mixed in the stopped-flow apparatus with a solution of NaY which contained sufficient $HClO_4$ to cause the pH of the reaction mixture to be in the desired range, usually between 1 and 2. The pH of the reaction mixture was obtained by measurement with a Beckman Model G pH meter.

Rates of all the reactions were determined spectrophotometrically by means of a stopped-flow apparatus, which consisted of a Beckman DU spectrophotometer to which was attached a rapid mixing device. These reactions were usually complete in 1 sec. or less. The change in percentage transmission with time at a convenient wave length as the reaction progressed was displayed on an oscilloscope. The oscilloscope trace was recorded permanently with a Polaroid camera. The reactions were made to go to completion by using an excess of reagent, usually more than ten times the complex concentration. The completeness of the reaction, as well as the nature of the product, was checked by recording the ultraviolet spectrum between 400 and 260 mμ on a Cary Model 11 or Beckman DK-2 spectrophotometer. Thus, the product of the reaction between $[Au(dien)Cl]Cl_2$ and bromide was identified by comparing a spectrum of the mixture with that of the known complex [Au-

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[1] For a review see F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

[2] R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954). It has just come to our attention that a detailed kinetic study on the reaction of $AuCl_4^-$ with ethylenediamine has been reported (P. Beran and A. A. Vlček, *Collection Czechoslov. Chem. Commun.*, **24**, 3572 (1959).

[3] W. H. Baddley, F. Basolo, H. B. Gray, C. Nölting, and A. J. Poë, *Inorg. Chem.*, **2**, 921 (1963).