

reaction. It will be seen that the rate constant for the Fe(II)–Ce(IV) reaction calculated in this manner is in good agreement with the observed value and that the rate constants for the Cr(II)–Fe(III), V(II)–Fe(III), Eu(II)–Fe(III), Cr(II)–Co(III), and V(II)–Co(III) reactions are consistent with the observed values. On the other hand, there is a large difference between the observed and calculated rate constants for the Fe<sup>2+</sup>–Co<sup>3+</sup> reaction. The reason for this discrepancy is not known. It may lie in the complexity of Co(III)

solutions or it may be that different spin restrictions obtain in the Fe<sup>2+</sup>–Co<sup>3+</sup> and Co<sup>2+</sup>–Co<sup>3+</sup> reactions. It is also possible that the Fe<sup>2+</sup>–Co<sup>3+</sup> reaction or the Co<sup>2+</sup>–Co<sup>3+</sup> reaction, or both, involve an atom transfer mechanism; the Marcus equations are not applicable to such reactions.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS, AND THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, NEW YORK

## Acidodiethylenetriaminegold(III) Complexes: Preparation, Solution Chemistry, and Electronic Structure

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The preparation of acidodiethylenetriaminegold(III) salts with the general formula [Au(dien)X]X<sub>2</sub> (dien = NH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>NH-C<sub>2</sub>H<sub>4</sub>NH<sub>2</sub> and X = Cl<sup>-</sup>, Br<sup>-</sup>) is reported. The complexes are acids in aqueous solution, ionizing a proton from one of the amine nitrogen atoms. The resulting conjugate bases, [Au(dien-H)X]X (dien-H = dien less one proton and X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>), have been isolated. Equilibrium constants for (N-H) ionization and for the hydrolysis are given. Electronic spectra of the [Au(dien)X]<sup>2+</sup> and [Au(dien-H)X]<sup>+</sup> complexes are assigned using a molecular orbital level classification.

### Introduction

Square-planar acidoammine complexes of the type [M(amine)<sub>n</sub>X<sub>4-n</sub>]<sup>(n-2)+</sup> (X = Cl<sup>-</sup>, Br<sup>-</sup>, etc.) where M = Pt<sup>2+</sup> and Pd<sup>2+</sup> are quite common and have played an important role in the experimental and theoretical development of coordination chemistry. However, there have been relatively few reports of compounds of this type for Au<sup>3+</sup>.<sup>5-12</sup>

This paper reports the general synthesis of complexes of Au<sup>3+</sup> with the tridentate ligand diethylenetriamine, which is abbreviated dien. An investigation of the aqueous solution chemistry of these compounds is discussed. The electronic structures of the [M(dien)X]<sup>n+</sup> (M = Pd<sup>2+</sup>, Pt<sup>2+</sup>, or Au<sup>3+</sup>) complexes are discussed in terms of molecular orbitals. Electronic spectra are assigned using a molecular orbital energy level scheme.

### Experimental

**Materials.**—The gold-containing starting material for the synthetic work was tetrachloroauric acid, which was freshly made for each preparation. In a typical experiment, 0.5 g. of fine gold powder (Engelhard Industries, Inc.) was added to a mixture of 5

ml. of concentrated HCl and 3 ml. of concentrated HNO<sub>3</sub>. The gold dissolved in a minute or so to give an orange solution. This solution was evaporated to 1–2 ml., 5 ml. of concentrated HCl was added, and the evaporation repeated. Again, 5 ml. of HCl was added and the evaporation repeated. Upon cooling, the solution crystallized to a solid mass of tetrachloroauric acid.

Diethylenetriamine (Union Carbide, technical grade) was distilled once, b.p. 204–208°. Other chemicals used were reagent grade.

**Analyses.**—The gold content was determined from the weight of the residue obtained by the ignition of a few hundredths of a gram of the compound in a microcrucible. Using this procedure, determination of gold in two of the compounds, [Au(dien-H)X]X (X = Cl<sup>-</sup>, Br<sup>-</sup>), gave poor results because these particular compounds tended to spatter when heated. This spattering was prevented by decomposing the compounds with a few drops of 30% hydrogen peroxide prior to ignition. The gold content was also determined by Miss H. Beck of the Chemistry Department, Northwestern University, who carried out the carbon and hydrogen elemental analyses. Several analyses were done by Microtech, Skokie, Ill.

**Preparation of Complexes.**—Each of the complexes reported was synthesized several times. Although some gold compounds are light-sensitive, most of these preparations were carried out under ordinary laboratory fluorescent lighting conditions. After preparation, the compounds were stored in the dark.

No attempt was made to ascertain the structures of these compounds. We make the reasonable assumption that they are square-planar complexes, as are the great majority of Au<sup>3+</sup> compounds. This assumption will be implied in the notation that is used throughout this paper. For example, the compound which analyzes as AuC<sub>6</sub>H<sub>12</sub>N<sub>3</sub>Cl<sub>3</sub> will be referred to as [Au(dien)Cl]Cl<sub>2</sub>.

**Synthesis of [Au(dien)Cl]Cl<sub>2</sub> and the Conjugate Base, [Au(dien-H)Cl]Cl.**—Tetrachloroauric acid was prepared from 6 g. of gold powder (30.5 mmoles). This was dissolved in 5 ml. of anhydrous ether and put in an ice bath. Thirteen ml. of dien (126 mmoles) was added to 20 ml. of anhydrous ether and also

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put in an ice bath. After cooling in ice for about 30 min., the tetrachloroauric acid solution was added dropwise from a medicine dropper, slowly with much manual stirring, to the amine solution. A yellow precipitate formed momentarily but changed rapidly to an orange viscous material as it was stirred. After all the  $\text{HAuCl}_4$  solution had been added, a viscous orange material settled to the bottom of the ethereal solution. The ether layer was decanted, 10 ml. more of ether was added and mixed with the orange viscous material, and the ether was decanted. This was repeated to remove excess amine. Reduction to metallic gold resulted if excess amine was left in contact with the orange viscous material for approximately 0.5 hr. Water (10 ml.) was then added to the orange viscous material, and it dissolved readily. With this orange solution still in the ice bath, concentrated  $\text{HCl}$ , also ice cold, was added dropwise with stirring. Occasionally, small pieces of ice were added to the reaction mixture. If too much heat was generated rapidly, reduction to gold occurred. As the pH of the reaction mixture decreased to *ca.* 6 (as tested with Alkacid test ribbon), an orange solid separated and quickly the entire contents of the beaker congealed. A small amount of this material was removed to a filter, washed with ethyl alcohol, and dried under vacuum overnight.

*Anal.* Calcd. for  $\text{AuC}_4\text{H}_{12}\text{N}_3\text{Cl}_2$ : C, 12.98; H, 3.27; N, 11.35; Au, 53.23. Found: C, 12.97; H, 3.32; N, 11.23; Au, 53.2.

To the remainder of the reaction mixture,  $\text{HCl}$  was added slowly. The orange suspension of the conjugate base slowly went into solution and fine, yellow crystals began to separate as the color of the solution changed from orange to green. This color change occurred at a pH of *ca.* 2 or 3. A total of 25 ml. of concentrated  $\text{HCl}$  was added; the time of addition was 2 hr. The yellow solid was collected on a filter, washed with a small quantity of ethanol, then with cold water, yielding 7 g. of fine, lime-green crystals. The green color is an indication of metallic gold contaminating the product. The green crystals were dissolved in 20 ml. of water at room temperature and filtered through a medium fritted glass funnel, leaving a small amount of metallic gold as a dark residue on the filter. To the clear, yellow filtrate was added 10 ml. of ethanol and a few drops of concentrated  $\text{HCl}$ , the pH of the solution being *ca.* 2. Upon being placed in an ice bath, fine yellow crystals formed immediately. After a few minutes, the product was collected on a filter, washed with a small amount of ice water, and dried under vacuum overnight. The yield was 4.25 g.

*Anal.* Calcd. for  $\text{AuC}_4\text{H}_{12}\text{N}_3\text{Cl}_3$ : C, 11.73; H, 3.20; Au, 48.10. Found: C, 12.03; H, 3.39; Au, 48.29.

The mother liquor was treated with 100 ml. of ethanol, yielding an additional 1.5 g. of material. The total yield was 53% of theoretical.

Another procedure was also used to prepare  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ . To 1.4 ml. of concentrated  $\text{HCl}$  was added 0.5 g. of tetrachloroauric acid (1.3 mmoles). This solution was cooled to  $0^\circ$ , then 1.1 ml. of dien (10.7 mmoles) was slowly added, drop by drop, with continuous shaking and cooling. A light yellow precipitate slowly separated and was removed by filtration. After being washed successively with small amounts of cold water and ether, the yellow solid was air dried. The yield was 50%.

*Anal.* Calcd. for  $\text{AuC}_4\text{H}_{12}\text{N}_3\text{Cl}_3$ : C, 11.73; H, 3.20; N, 10.3; Au, 48.10. Found: C, 12.0; H, 3.47; N, 10.4; Au, 47.4.

**Synthesis of  $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$ .**—Two grams of  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  (4.9 mmoles) was dissolved in 6 ml. of water. On adding 4 g. of powdered  $\text{NaBr}$  (39 mmoles) to the yellow solution, an orange precipitate formed immediately. After cooling in an ice bath for 1 hr., the precipitate was collected on a filter and washed with ice water. This solid was then placed in 40 ml. of water (at room temperature) containing 1 g. of  $\text{NaBr}$ , but not quite all of it dissolved. The mixture was filtered, and to the filtrate was added several drops of  $\text{HClO}_4$ . Then 60 ml. of 1:1 ethanol-diethyl ether was added and the solution was placed in an ice bath. Fine, shiny orange crystals began to separate slowly. These were collected on a filter and washed successively with ice-cold water,

ethanol, and anhydrous ether. After drying under vacuum for 3 hr. a yield of 1.2 g. was obtained.

*Anal.* Calcd. for  $\text{AuC}_4\text{H}_{12}\text{N}_3\text{Br}_3$ : Au, 36.5. Found: Au, 36.6.

The compound was also prepared by treating the orange solution formed from the reaction of dien and  $\text{HAuCl}_4$  with  $\text{NaBr}$ , followed by acidification with  $\text{HBr}$ . A third procedure used to prepare  $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$  was to dissolve  $\text{HAuCl}_4$  in  $\text{HBr}$ , and then add dien at  $0^\circ$ .

**Synthesis of  $[\text{Au}(\text{dien-H})\text{Br}]\text{Br}$ .**—To the orange viscous material that resulted from the reaction of  $\text{HAuCl}_4$  (prepared from 0.5 g. of Au; 2.5 mmoles) with dien (after the ether had been decanted) was added 2.5 g. of powdered  $\text{NaBr}$  (24 mmoles) and 2 ml. of water. The pH at this point was *ca.* 9 and  $\text{HClO}_4$  was added slowly with stirring. As the acid came in contact with the solution, a bright red color appeared, but disappeared with stirring. At a pH of *ca.* 6–8 an orange solid separated. After standing in an ice bath for 30 min., the mixture was filtered and washed with ice water, then with ether, and dried under vacuum overnight. The yield of orange-yellow material was 0.25 g.

*Anal.* Calcd. for  $\text{AuC}_4\text{H}_{12}\text{N}_3\text{Br}_2$ : C, 10.47; H, 2.64. Found: C, 10.53; H, 2.86.

**Synthesis of  $[\text{Au}(\text{dien-H})\text{I}]\text{I}$ .**—To the orange viscous material, dissolved in 2 ml. of water, that resulted from the reaction of  $\text{HAuCl}_4$  (prepared from 0.5 g. of gold; 2.5 mmoles) and dien was added 5 ml. of water containing 4.2 g. of  $\text{NaI}$  (28 mmoles). An orange precipitate formed immediately. The precipitate was collected on a filter and washed with water and anhydrous ether. After drying under vacuum for 3 hr., the material weighed 1 g., which is a yield of 72%.

*Anal.* Calcd. for  $\text{AuC}_4\text{H}_{12}\text{N}_3\text{I}_2$ : C, 8.69; H, 2.19; Au, 35.63. Found: C, 9.02; H, 2.39; Au, 35.60.

Attempts to prepare the conjugate acid,  $[\text{Au}(\text{dien})\text{I}]\text{I}_2$ , by treating an aqueous solution of  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  with excess  $\text{NaI}$ , yielded a black amorphous solid, the analysis of which was not consistent with the desired product.

**Synthesis of  $[\text{Au}(\text{dien})\text{Cl}][\text{AuCl}_4]\cdot 2\text{H}_2\text{O}$ .**—To 5 ml. of water was added 1 g. of dien·3 $\text{HCl}$  (5 mmoles) and 0.5 ml. of dien (5 mmoles). This mixture was placed in an ice bath and to it was added 5 ml. of an aqueous solution of  $\text{HAuCl}_4$ , which was prepared from 1 g. of gold (5 mmoles). An amorphous, canary yellow precipitate formed immediately. The product was collected on a filter and washed successively with cold water acidified with  $\text{HCl}$ , ethanol, and diethyl ether. After drying under vacuum for 3 hr., the yield was 0.5 g.

*Anal.* Calcd. for  $\text{Au}_3\text{C}_4\text{H}_{16}\text{N}_3\text{Cl}_9\text{O}$ : C, 4.66; H, 1.47; Au, 57.31. Found: C, 5.77; H, 1.56; Au, 57.19.

**Synthesis of  $[\text{dienH}_2][\text{AuCl}_4]\cdot 2\text{H}_2\text{O}$ .**—Tetrachloroauric acid was prepared from 0.25 g. of gold (1.2 mmoles) and dissolved in 5 ml. of water. To 5 ml. of water was added 0.05 ml. of dien (0.5 mmole) and 2 ml. of concentrated  $\text{HCl}$ . The acidified amine solution was added to the  $\text{HAuCl}_4$  solution. No perceptible change occurred. However, after cooling in an ice bath, shiny needle-like yellow crystals began to form. After 1 hr. in the ice bath, the crystals were collected and washed with ice water, ethanol, and anhydrous ether in that order, then air dried for 48 hr.

*Anal.* Calcd. for  $\text{Au}_3\text{C}_4\text{H}_{16}\text{N}_3\text{Cl}_9\text{O}$ : C, 4.21; H, 1.59; Au, 51.81. Found: C, 4.59; H, 1.63; Au, 51.69.

**Other Compounds.**—The method of Block and Bailar<sup>10</sup> was used to prepare  $[\text{Au}(\text{en})_2]\text{Cl}_3$ . Several other compounds used in this study,  $[\text{M}(\text{dien})\text{X}]\text{X}$  ( $\text{M} = \text{Pt}^{2+}, \text{Pd}^{2+}$ ;  $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$ ), were previously prepared.<sup>13</sup>

**Visible and Ultraviolet Spectra.**—The visible and ultraviolet absorption spectra were measured with Beckman DK-2, Cary 14, and Cary 11 spectrophotometers, using 1-cm. quartz cells. The concentrations are listed in the captions to the figures showing the spectra.

**Potentiometric Titrations.**—These were carried out in a jacketed beaker through which water circulated from a constant

(13) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).

temperature bath at  $25.0 \pm 0.1^\circ$ . A magnetic stirrer was used to agitate the solution, but stirring was stopped when the readings were taken. A Beckman pH Meter, Model G, in conjunction with a glass electrode was used to measure the pH. The meter was standardized immediately prior to the titration with a solution saturated with potassium bitartrate (Baker Analyzed Reagent) at pH 3.56, and with Beckman buffer solution at pH 7.0. A 5 ml. microburet was used to add the titrant. Water used to dissolve the complex and to prepare the titrant solutions was boiled for 2 hr., then flushed with nitrogen to remove  $\text{CO}_2$ . The NaOH solutions were prepared with  $\text{CO}_2$ -free water and standardized in duplicate with potassium acid phthalate either immediately before or immediately after the titration was performed. Solutions of  $\text{HClO}_4$  were standardized with standard NaOH solution. The initial volume of the solution to be titrated was usually 100 ml. Volume change during the titration was usually less than 10%. The time required for a titration was 30 min. or less. End points were calculated from  $\Delta\text{pH}/\Delta\text{ml}$ . data. Exact data for a number of titrations are given in Table I.

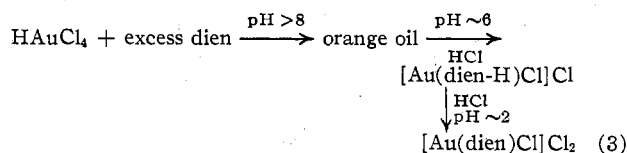
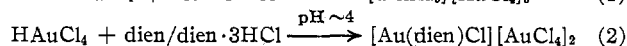
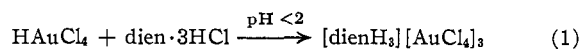
TABLE I  
POTENTIOMETRIC TITRATION DATA<sup>a</sup> AT  $25^\circ$ ; IONIC STRENGTH = 0.5

[complex] $\times 10^3$ , moles/l.	pH <sub>0.5</sub>	pH <sub>1.5</sub>	Salt added
(A) $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$			
0.487	3.9	6.2	$\text{LiClO}_4$
1.209	4.0	6.5	$\text{NaClO}_4$
2.037	4.0	6.6	$\text{NaClO}_4$
0.464	4.7	...	$\text{NaCl}$
1.643	4.7	...	$\text{NaCl}$
(B) $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$			
1.521	4.6	7.5	$\text{NaClO}_4$
1.476	4.5	7.5	$\text{NaClO}_4$
1.517	5.2	...	$\text{NaBr}$
(C) $[\text{Au}(\text{en})_2]\text{Cl}_3$			
1.714	6.3	...	$\text{NaClO}_4$
2.444	7.2	...	$\text{KCl}$

<sup>a</sup> pH<sub>0.5</sub> is the pH of the solution being titrated when 0.5 mole of  $\text{OH}^-$  per mole of complex had been added and pH<sub>1.5</sub> is the pH when 1.5 moles of  $\text{OH}^-$  per mole of complex had been added.

### Results and Discussion

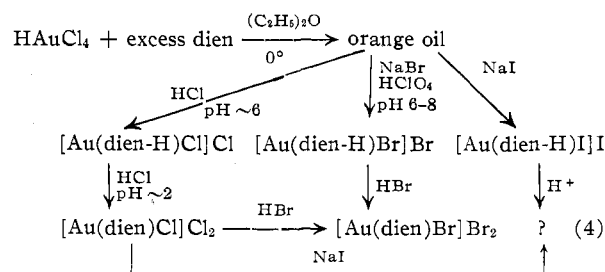
The reaction between  $\text{HAuCl}_4$  and dien yielded several different products. The product obtained depends on the relative proportions of the two reagents and the pH of the reacting mixture. These reactions are represented by eq. 1, 2, and 3.



Reaction 1 yields the so-called "normal" tetrachloroaurate. This general type of reaction has long been used in organic chemistry as a means of preparing solid derivatives of amines. Reaction 2 yields a product somewhat analogous to the "Magnus" salts in  $\text{Pt}^{2+}$  and  $\text{Pd}^{2+}$  chemistry. In reaction 3, the product first obtained is an amido complex, which in turn yields the ammine, or conjugate acid, on careful acidification. Amido complexes have not been reported for  $\text{Pt}^{2+}$  or

$\text{Pd}^{2+}$  in aqueous solution,<sup>14</sup> and probably do not exist, but are possible with  $\text{Au}^{3+}$  due to its larger positive charge. Block and Bailar<sup>10</sup> reported the isolation of the amido complex  $[\text{Au}(\text{en-H})\text{en}]\text{Br}_2$  as well as its conjugate acid.

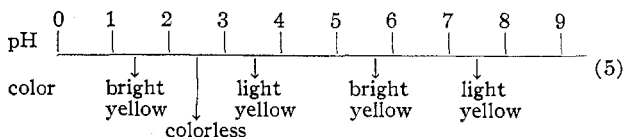
The preparation of amido and amine complexes of  $\text{Au}^{3+}$  in this investigation is summarized by reaction scheme 4.



The orange oil shown in this scheme has not been identified. When treated with sodium tetraphenylboron, it yielded a yellow solid that decomposed before it was possible to obtain an elemental analysis. Attempts to isolate  $[\text{Au}(\text{dien})\text{I}]\text{I}_2$  resulted in the formation of a black material whose elemental analysis was not consistent with any expected product. This black material decomposed on standing at room temperature.

The amine complexes,  $[\text{Au}(\text{dien})\text{X}]\text{X}_2$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ), appear to be stable indefinitely (no decomposition in a year) in the solid state, whereas the amido complexes,  $[\text{Au}(\text{dien-H})\text{X}]\text{X}$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ), begin to decompose in a week or so after preparation. The amine complexes discolored in several days if they had not been previously purified by recrystallization. These complexes are sensitive to heat above  $40-50^\circ$ .

The aqueous solution chemistry of these complexes includes both acid-base and hydrolytic equilibria. For example, consider the complex which analyzes in the solid state as  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ . The color changes which occur in *ca.*  $10^{-3} M$  aqueous solution as the pH is varied are shown below



In view of the facts already known about the aqueous chemistry of  $\text{Au}^{3+}$  complexes and the data to be discussed below, these observations may be explained by processes that are depicted in Fig. 1. Aquo species, *i.e.*,  $[\text{Au}(\text{dien})(\text{OH}_2)]^{3+}$ , are not included in the scheme as hydrolysis products because such aquo species probably do not exist quantitatively in aqueous solution for cationic species of  $\text{Au}^{3+}$ , except perhaps in very acidic solution. Bjerrum<sup>15</sup> has noted that aquo species are not present in aqueous solutions of the anionic  $\text{AuCl}_4^-$  complex.

(14) Amido complexes of  $\text{Pt}^{2+}$  and  $\text{Pd}^{2+}$  have been isolated from liquid ammonia. See G. W. Watt, L. E. Sharif, and E. P. Helvenston, *Inorg. Chem.*, **1**, 6 (1962), and references cited therein.

(15) N. Bjerrum, *Bull. Soc. Chim. Belges*, **57**, 432 (1948).

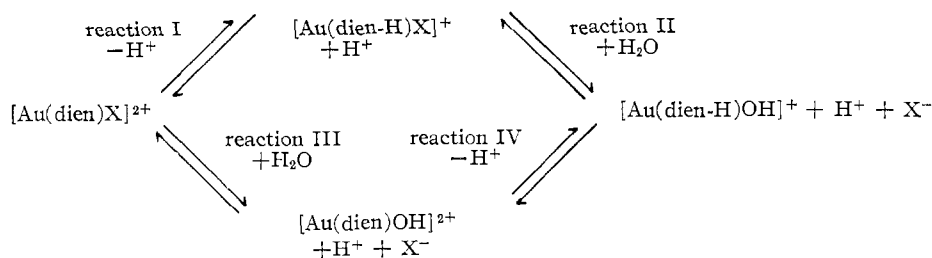


Fig. 1.—Equilibria occurring in aqueous solutions of  $[\text{Au}(\text{dien})\text{X}]\text{X}_2$  ( $\text{X} = \text{Cl}^-, \text{Br}^-$ ) in the pH range 2–10.

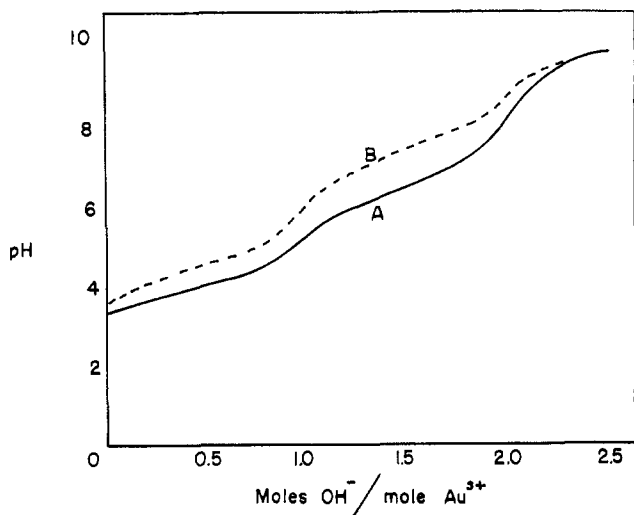


Fig. 2.—Curve A: Potentiometric titration curve of 0.1209 mmole of  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  with 0.02433  $M$   $\text{NaOH}$  at  $24.9^\circ$ ;  $\mu = 0.5$  with  $\text{NaClO}_4$ . Curve B: Potentiometric titration curve of 0.1478 mmole of  $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$  with 0.02433  $M$   $\text{NaOH}$  at  $24.9^\circ$ ;  $\mu = 0.5$  with  $\text{NaClO}_4$ .

An understanding of the equilibria shown in Fig. 1 was obtained by glass electrode and spectral measurements. Curve A in Fig. 2 is the potentiometric titration curve of  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  (ionic strength was 0.5 with  $\text{NaClO}_4$ ). One observes two distinct end points, the first one occurring after the addition of exactly one equivalent of hydroxide ion per mole of  $\text{Au}^{3+}$ , and the second end point occurring after the addition of exactly two moles of hydroxide ion per mole of  $\text{Au}^{3+}$ . Referring to Fig. 1 these curves may be explained by a sequence involving reactions I and II in which the first end point is due to the ionization of a proton from a coordinated nitrogen atom and the second end point is due to the hydrolysis of the covalent halide.<sup>16</sup>

Reactions III and IV may also explain the titration curve. Thus the first end point would be due to the hydrolysis of  $[\text{Au}(\text{dien})\text{X}]^{2+}$  (reaction III) and the second end point would be due to the titration of the acid  $[\text{Au}(\text{dien})\text{OH}]^{2+}$  (reaction IV). If the sequence involving reactions III and IV were correct, one would expect that  $\text{pH}_{1.5}$  (that is, the pH midway between the first and second end point) would be the same in curve A and curve B of Fig. 2, since  $[\text{Au}(\text{dien})\text{OH}]^{2+}$  would be the acid titrated for the second end point regardless

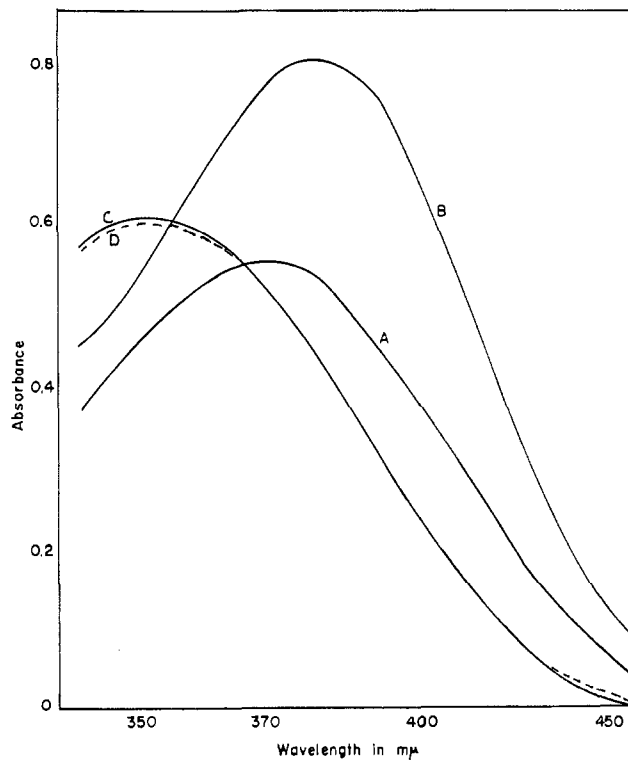


Fig. 3.—Spectrum A: Absorption spectrum of  $3.95 \times 10^{-4} M$   $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  plus one equivalent of  $\text{NaOH}$ . Spectrum B: Absorption spectrum of  $4.01 \times 10^{-4} M$   $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$  plus one equivalent of  $\text{NaOH}$ . Spectrum C: Absorption spectrum of  $3.95 \times 10^{-4} M$   $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  plus two equivalents of  $\text{NaOH}$ . Spectrum D: Absorption spectrum of  $4.01 \times 10^{-4} M$   $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$  plus two equivalents of  $\text{NaOH}$ .

of whether one started initially with  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  or  $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$ . Since  $\text{pH}_{1.5(\text{Cl})}$  is 6.5 and  $\text{pH}_{1.5(\text{Br})}$  is 7.5, a sequence involving reactions I and II is favored over a sequence involving reactions III and IV. Further proof of this is offered by the absorption spectra shown in Fig. 3, where one observes that the spectrum of  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  plus one equivalent amount of  $\text{OH}^-$  (curve A) is different from that of  $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$  plus one equivalent amount of  $\text{OH}^-$  (curve B). Clearly, the product obtained on adding an equivalent of  $\text{OH}^-$  to either the chloro or bromo complex is not  $[\text{Au}(\text{dien})\text{OH}]^{2+}$ , otherwise the spectra would be identical. After the addition of two equivalent amounts of  $\text{OH}^-$  to the bromo and chloro complexes, the spectra are identical. Thus, curves C and D of Fig. 3 are presumably the spectrum of  $[\text{Au}(\text{dien-H})\text{OH}]^+$ . Curves C and D in Fig. 3 also rule out the possibility that  $[\text{Au}(\text{dien})\text{X}]^{2+}$  is a dibasic acid, yielding first  $[\text{Au}(\text{dien-H})\text{X}]^+$  then  $[\text{Au}(\text{dien-2H})\text{X}]^0$ . If  $[\text{Au}(\text{dien})\text{X}]^{2+}$  were a di-

(16) Preliminary kinetic studies of substitution reactions of these complexes show that the covalent halide is completely substituted for in a matter of a few seconds at  $25^\circ$ . Thus, in the course of a potentiometric titration the hydrolysis equilibrium is established very rapidly.

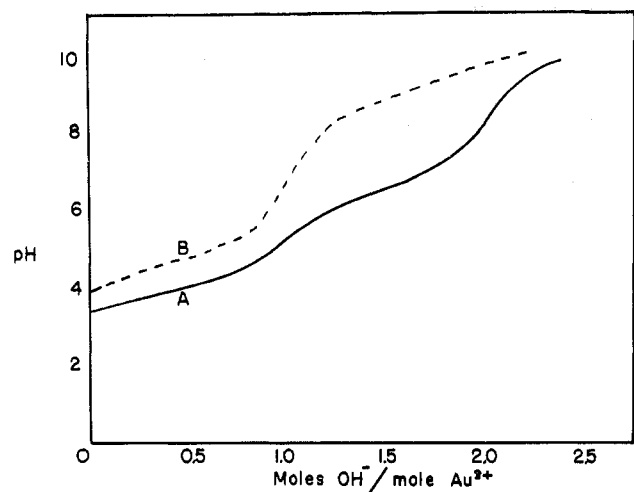
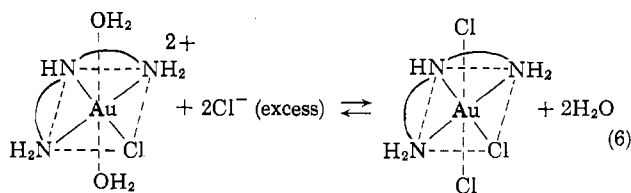


Fig. 4.—Curve A: Potentiometric titration of 0.1209 mmole of  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  with 0.02433  $M$   $\text{NaOH}$  at  $24.9^\circ$ ;  $\mu = 0.5$  with  $\text{NaClO}_4$ . Curve B: Potentiometric titration of 0.1643 mmole of  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  with 0.08158  $M$   $\text{NaOH}$  at  $25.0^\circ$ ;  $\mu = 0.51$  with  $\text{NaCl}$ .

basic acid, the spectra would be different for  $X = \text{Cl}^-$  and  $X = \text{Br}^-$ .

Further insight into the aqueous chemistry of these complexes was obtained by titrating  $[\text{Au}(\text{dien})\text{X}]\text{X}_2$  ( $X = \text{Cl}^-, \text{Br}^-$ ) in the presence of  $0.5 M X^-$ . If the second break in the titration curves described above is due to a hydrolysis of the covalent halide as we have suggested, then one might expect that a titration carried out in excess  $X^-$  would show only one end point since the hydrolysis equilibrium would be suppressed. Figure 4 shows the titration curve of  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  in the presence of  $0.5 M \text{ClO}_4^-$  (curve A) and in the

presence of  $0.5 M \text{Cl}^-$  (curve B). In curve B one observes only one end point, and this occurs after the addition of one mole of hydroxide per mole of  $\text{Au}^{3+}$ . One also observes from Fig. 4 that  $\text{pH}_{0.5}$  (that is,  $\text{p}K_a$  of  $[\text{Au}(\text{dien})\text{Cl}]^{2+}$ ) is 4.0 in  $0.5 M \text{ClO}_4^-$  but 4.7 in  $0.5 M \text{Cl}^-$ . Ostensibly, the lower pH values in the absence of excess chloride may be ascribed to the hydrolysis reaction (reaction III, Fig. 1). However, an alternative explanation is possible. Spectra of  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  solutions in the pH range 2.46–4.12 in the presence of  $0.1 M \text{Cl}^-$  and  $0.1 M \text{ClO}_4^-$  are shown in Fig. 5. As would be expected, isosbestic points are observed in the solutions with excess halide, since the only species presumably present are  $[\text{Au}(\text{dien})\text{Cl}]^{2+}$  and  $[\text{Au}(\text{dien}-\text{H})\text{Cl}]^+$ . Isosbestic points occur also in the  $0.1 M \text{ClO}_4^-$  solutions, but here the isosbestic points are at slightly different wave lengths and the intensities of absorption are different from the solutions containing excess chloride. The isosbestic points in the  $0.1 M \text{ClO}_4^-$  solutions rule out the presence of a third species such as  $[\text{Au}(\text{dien})\text{OH}]^{2+}$ . We suggest that these differences in  $\text{p}K_a$  values and spectra are due to axial interactions such as shown by eq. 6.



Such an interaction would be expected to lower the acidity of the complex, since the effective positive charge would be decreased. Further proof of this effect

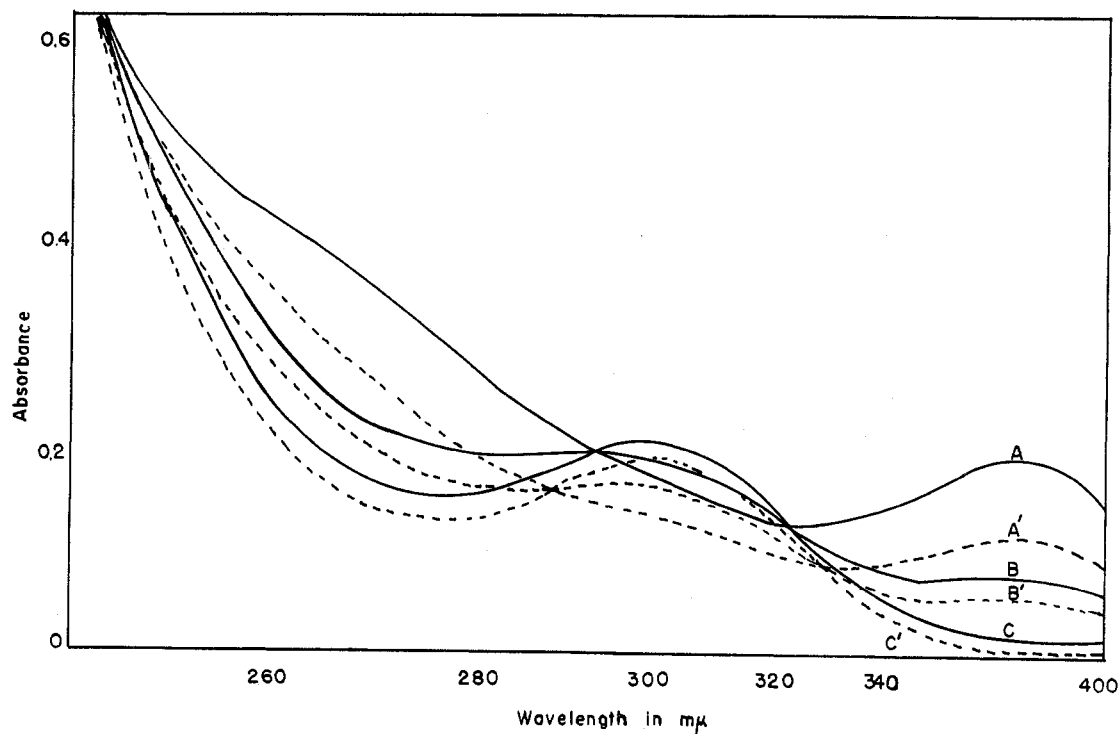


Fig. 5.—Absorption spectra of  $2.47 \times 10^{-4} M$   $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  in the pH range 2.46–4.12: —, in  $0.1 M \text{NaCl}$ ; ---, in  $0.1 M \text{LiClO}_4$ ; pH adjusted with  $\text{HClO}_4$ ; pH of solutions: A, 4.12; B, 3.48; C, 2.48; A', 4.00; B', 3.42; C', 2.46.

of excess anion on the  $pK_a$  of  $Au^{3+}$  cationic complexes is afforded by the  $pK_a$  values of  $[Au(en)_2]^{3+}$  in 0.5 M  $ClO_4^-$  and 0.5 M  $Cl^-$ , which are 6.3 and 7.2, respectively.

The  $pK_a$  values for several complexes are summarized in Table II. Complete potentiometric data from which these values were obtained are listed in Table I.

TABLE II  
ACID STRENGTHS OF SOME GOLD(III) COMPLEXES

Complex	$pK_a$ (in 0.5 M $ClO_4^-$ )	$pK_a$ (in 0.5 M $X^-$ )
$[Au(dien)Cl]Cl_2$	4.0	4.7 (X = $Cl^-$ )
$[Au(dien)Br]Br_2$	4.5	5.2 (X = $Br^-$ )
$[Au(dien)OH](NO_3)_2^a$	5.8	...
$[Au(en)_2]Cl_3$	6.3	7.2 (X = $Cl^-$ )

<sup>a</sup> The  $pK_a$  of  $[Au(dien)OH]^{2+}$  was determined by dissolving  $[Au(dien)Cl]Cl_2$  in water, adding two equivalents of hydroxide ion, and passing the resulting solution through an IRA-400 anion-exchange resin in the nitrate form to remove chloride ion. The effluent, presumably a solution of  $[Au(dien-H)OH](NO_3)$ , was then titrated with  $HClO_4$ .

It is interesting to note that the  $pK_a$  values of  $[Au(dien)X]^{2+}$  (X =  $Cl^-$ ,  $Br^-$ ,  $OH^-$ ) are in the same order of decreasing acidity as was observed for some  $Pt^{4+}$  complexes. The  $pK_a$  values<sup>17</sup> for  $[Pt(NH_3)_6X]^{3+}$  were found to be 8.1, 8.3, and 9.5 for X =  $Cl^-$ ,  $Br^-$ , and  $OH^-$ , respectively.

The  $pK_a$  value of  $[Au(dien)X]^{2+}$  relative to the  $pK_a$  of  $[Au(en)_2]^{3+}$  should be discussed. One might expect  $[Au(en)_2]^{3+}$  with a larger cationic charge to be more acidic than  $[Au(dien)X]^{2+}$ , which is the reverse of what is found. It is to be noted that even though the total positive charge on the en complex is larger, the partial positive charge per nitrogen atom is essentially the same, since there is one less nitrogen atom in the dien complex. The total positive charge on the complex is not the primary criterion in determining the relative acid strengths of these two species. That the cationic charge of an ammine complex does not have a marked effect on acidity is shown in  $Pt^{4+}$  complexes, where the  $pK_a$  values of  $[Pt(NH_3)_6]^{4+}$  and  $[Pt(NH_3)_6Cl]^{3+}$  are 7.9 and 8.1, respectively.<sup>17</sup>

Chelation in metal amines seems to have a more important effect than does cationic charge in influencing acidity. One example of this is the  $pK_a$ <sup>17</sup> of 5.5 for  $[Pt(en)_3]^{4+}$ , which is to be compared with a  $pK_a$  of 7.9 for  $[Pt(NH_3)_6]^{4+}$ . A chelate effect may be responsible for  $[Au(dien)X]^{2+}$  being a stronger acid than is  $[Au(en)_2]^{3+}$ . This effect of chelation on acidity has been explained in terms of a decreasing energy of solvation<sup>18</sup> as chelation is increased. In addition, electrostatic effects should be considered, and in discussing these effects in metal amines, it is convenient to use the terminology that previous workers used in regard to organic carboxylic acids.<sup>19</sup> Electrostatic effects were

divided into "inductive effects" which are transmitted through a chain of atoms and "field effects" which are transmitted through empty space or solvent molecules. In the complex  $[Au(dien)X]^{2+}$ , transmission of positive charge in the coordinated amine would be *via* the carbon chain. If one assigns a dielectric constant of about 2 (corresponding to paraffin hydrocarbons) to the carbon chain, it is easy to visualize how transmission of positive charge is facilitated in  $[Au(dien)X]^{2+}$  relative to  $[Au(en)_2]^{3+}$ . In the former system, transmission of positive charge is entirely by way of the carbon chain with its low dielectric constant, whereas in the latter system part of the charge must be transmitted *via* solvent molecules (water in this case) which have a much higher dielectric constant. It has not been shown experimentally from which nitrogen atom the proton is ionizing in  $[Au(dien)X]^{2+}$ . It is quite reasonable to assume that ionization is from the central nitrogen atom, that is, the nitrogen atom *trans* to X. When dien is coordinated to  $H^+$  instead of  $Au^{3+}$ , it is the central nitrogen atom from which the proton is lost, as evidenced by the  $pK_a$  values<sup>20</sup> of 4.61 for  $dienH_3^{3+}$ , 9.21 for  $dienH_2^{2+}$ , and 9.98 for  $dienH^+$ . In summary,  $[Au(dien)X]^{2+}$  is a stronger acid than  $[Au(en)_2]^{3+}$  because chelation is more important in influencing relative acidity in complexes than is the total charge on the complex.

Approximate values for the hydrolytic equilibria (reactions II and III in Fig. 1) have been obtained. The equilibrium constants are shown in Table III, whereas the data from which they were obtained was included in Table I. From Table III, one observes that for the systems  $[Au(dien)X]^{2+}$  or  $[Au(dien-H)X]^+$  (X =  $Cl^-$ ,  $Br^-$ ,  $OH^-$ ), the stability decreases in the order  $OH^- > Br^- > Cl^-$ , which is the same order as that observed for  $Pt^{2+}$  complexes.<sup>21</sup>

TABLE III  
HYDROLYTIC EQUILIBRIUM CONSTANTS AT 25°;  $\mu = 0.5$  WITH  $ClO_4^-$

A.	$[Au(dien-H)X]^+ + OH^- \xrightleftharpoons{K_{OH(X)}} [Au(dien-H)OH]^+ + X^-$
	X = $K_{OH(X)}^a$
	$Cl^-$ 10 <sup>6</sup>
	$Br^-$ 10 <sup>4.1</sup>
B.	$[Au(dien)X]^{2+} + H_2O \xrightleftharpoons{K_{H_2O(X)}} [Au(dien)OH]^{2+} + H^+ + X^-$
	X = $K_{H_2O(X)}^b$
	$Cl^-$ $6 \times 10^{-8}$
	$Br^-$ $4 \times 10^{-9}$

<sup>a</sup> The values of  $K_{OH(X)}$  were calculated from the expression

$$K_{OH(X)} = \frac{\{[Au(dien-H)OH]^+\} \{X^-\}}{\{[Au(dien-H)X]^+\} \{OH^-\}}$$

by assuming that at  $pH_{1.5}$  in the titration curve (half-way between the first and second end point) the concentration of  $[Au(dien-H)OH]^+$  equals the concentration of  $[Au(dien-H)X]^+$ . The concentration of  $X^-$  at  $pH_{1.5}$  equals 2.5 times the original complex concentration, since there are two ionic halides in the complex. The hydroxide concentration was obtained from the titration curve at  $pH_{1.5}$ . <sup>b</sup> Calculated from the equation

$$K_{H_2O(X)} = K_a(X)K_{OH(X)}K_w/K_a(OH)$$

(17) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 383.

(18) Reference 17, p. 392.

(19) J. D. Roberts and W. T. Moreland, *J. Am. Chem. Soc.*, **75**, 2167 (1953).

(20) J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 985 (1950).

(21) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

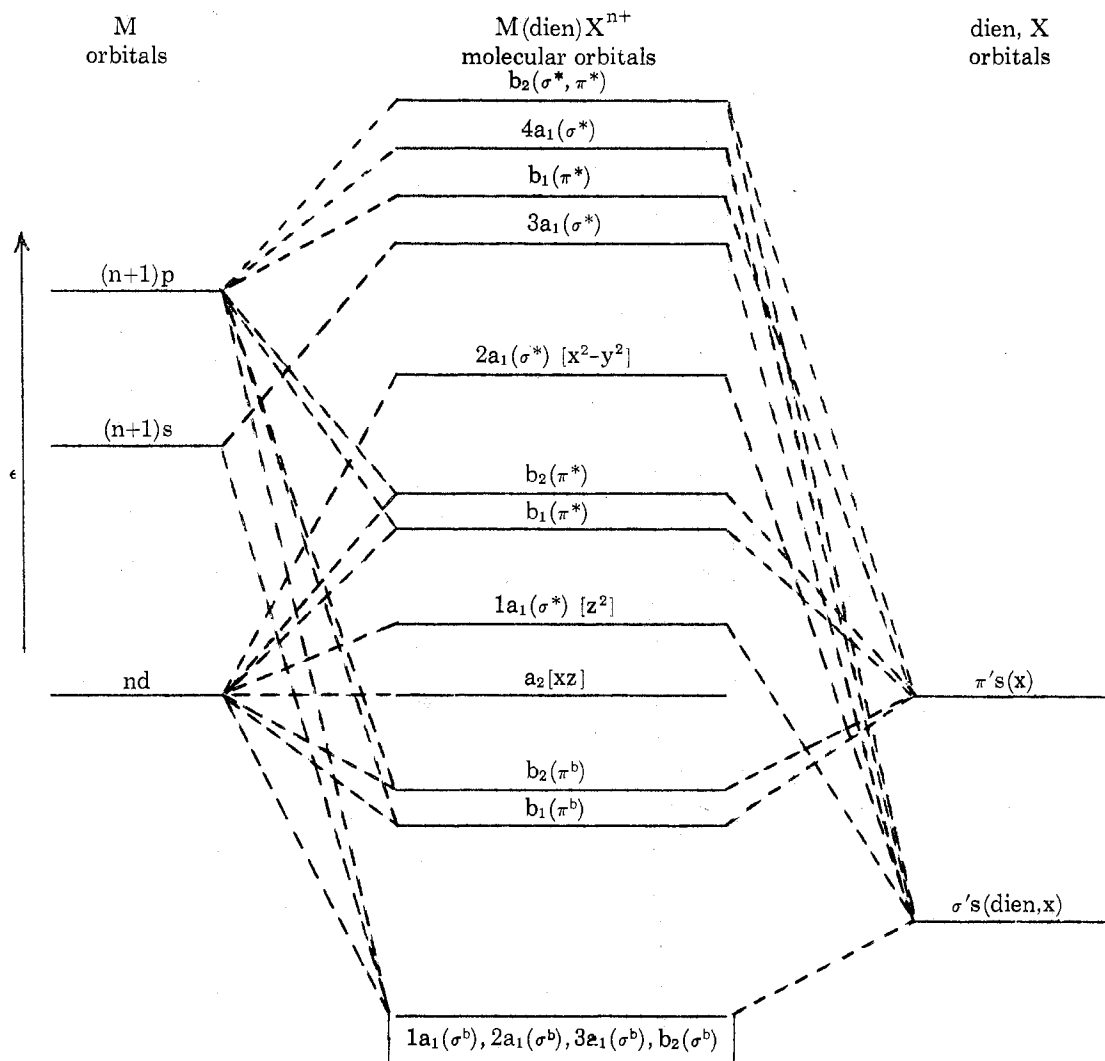


Fig. 6.—Molecular orbital energy level scheme for  $[M(\text{dien})\text{X}]^{n+}$  complexes.

#### Electronic Spectra of $[M(\text{dien})\text{X}]^{n+}$ Complexes.—

The  $[M(\text{dien})\text{X}]^{n+}$  complexes ( $M = \text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$ , or  $\text{Au}^{3+}$ ) are considered to be square-planar, with effectively  $C_{2v}$  symmetry. The four ligand atoms (3N and X) are aligned along the  $x$  and  $y$  axes, with the  $x$  axis taken for  $C_2$ . There are four ligand  $\sigma$ -valence orbitals (one from each N, one from X) and two  $\pi$ -valence orbitals (both from X). The metal has the usual  $nd$ ,  $(n+1)s$ , and  $(n+1)p$  valence orbitals.

A molecular orbital energy level scheme for the  $[M(\text{dien})\text{X}]^{n+}$  complexes is shown in Fig. 6. This level scheme was arrived at by modifying the general M.O. scheme<sup>22</sup> ( $D_{4h}$  symmetry with full  $\sigma$ - and  $\pi$ -bonding) for  $C_{2v}$  symmetry and limited  $\pi$ -bonding. The ground state of the  $[M(\text{dien})\text{X}]^{n+}$  complexes is

$$[1a_1(\sigma^b)]^2[2a_1(\sigma^b)]^2[3a_1(\sigma^b)]^2[b_2(\sigma^b)]^2[b_1(\pi^b)]^2[b_2(\pi^b)]^2 \\ [a_2]^2[1a_1(\sigma^*)]^2[b_1(\pi^*)]^2[b_2(\pi^*)]^2 = {}^1A_1$$

The  $[M(\text{dien})\text{X}]^{n+}$  complexes show a single absorption band of intermediate intensity ( $\epsilon$  range is 200–2000) in the 25,000–40,000  $\text{cm}^{-1}$  region. Following the level scheme, the band is assigned  $b_2b_1(\pi^*) \rightarrow 2a_1(\sigma^*)$  [ ${}^1A_1 \rightarrow {}^1B_1, {}^1B_2$ ]. The transition involves transferring an

electron from a  $\pi$ -molecular orbital, delocalized over M and X, to the  $2a_1(\sigma^*)$  orbital, which is essentially the  $nd_{x^2-y^2}$  metal orbital.

The positions of the first maximum in the electronic absorption spectra of  $[M(\text{dien})\text{X}]^{n+}$  complexes are given in Table IV. For any M, the band increases in energy in the X order  $\text{I} < \text{Br} < \text{Cl}$ . This is consistent with the assignment of the transition as a partial charge-

TABLE IV  
THE LONG WAVE LENGTH ELECTRONIC TRANSITION IN  
 $[M(\text{dien})\text{X}]^{n+}$  COMPLEXES

Complex	$\tau_{\text{max}}$ , Å.	$\nu_{\text{max}}$ , $\text{cm}^{-1}$	$b_1, b_2(\pi^*) \rightarrow 2a_1(\sigma^*) [x^2 - y^2]$	
			${}^1A_1 \rightarrow {}^1B_1, {}^1B_2$	$\epsilon_{\text{max}}$
$[\text{Pd}(\text{dien})\text{Cl}]^+$	3380	29,590		500
$[\text{Pd}(\text{dien})\text{Br}]^+$	3450	28,990		450
$[\text{Pd}(\text{dien})\text{I}]^+$	3700	27,030		500
$[\text{Pt}(\text{dien})\text{Cl}]^+$	2700	37,040		275
$[\text{Pt}(\text{dien})\text{Br}]^+$	2750	36,360		250
$[\text{Pt}(\text{dien})\text{I}]^+$	3000	33,330		500
$[\text{Au}(\text{dien})\text{Cl}]^{2+ a}$	3020	33,110		815
$[\text{Au}(\text{dien})\text{Br}]^{2+ a}$	3400	29,410		510
$[\text{Au}(\text{dien})\text{I}]^{2+ b}$	3830	26,110		1800

<sup>a</sup> Spectrum at pH 2.5–3.0. <sup>b</sup> Tentative solution spectrum. The complex was not isolated as a pure substance—see text.

TABLE V  
 ELECTRONIC SPECTRA OF  $[\text{Au}(\text{dien-H})\text{X}]^+$  COMPLEXES

Complex	$b_1, b_2(\pi^*) \rightarrow 2a_1(\sigma^*)$			$2p_\pi(\text{dien-H}) \rightarrow 2a_1(\sigma^*)$		
	$\tau_{\text{max}}$ , Å.	$\nu_{\text{max}}$ , $\text{cm.}^{-1}$	$\epsilon_{\text{max}}$	$\tau_{\text{max}}$ , Å.	$\nu_{\text{max}}$ , $\text{cm.}^{-1}$	$\epsilon_{\text{max}}$
$[\text{Au}(\text{dien-H})\text{Cl}]^{\text{a}+}$	2630	38,020	2930	3700	27,030	1900
$[\text{Au}(\text{dien-H})\text{Br}]^{\text{b}+}$	2840	35,210	2340	3800	26,320	2180
$[\text{Au}(\text{dien-H})\text{OH}]^{\text{c}+}$	Not observed			3500	28,570	1680

<sup>a</sup> Equivalent concentrations of  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  and  $\text{OH}^-$ , with 0.5 M  $\text{Cl}^-$ . <sup>b</sup> Equivalent concentrations of  $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$  and  $\text{OH}^-$ , with 0.5 M  $\text{Br}^-$ . <sup>c</sup> Complex present in a solution originally containing  $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$  at pH 11.5.

transfer process, since the stability of  $\pi(\text{X})$  is expected to increase in the order  $\pi(\text{I}) < \pi(\text{Br}) < \pi(\text{Cl})$ .

The charge-transfer assignment is also indicated from a comparison of analogous  $\text{Pt}^{2+}$  and  $\text{Au}^{3+}$  complexes. Thus the band for any given X complex shifts to lower energy in going from  $\text{Pt}^{2+}$  to the better electron acceptor,  $\text{Au}^{3+}$ . This type of evidence has been used to assign ligand  $\rightarrow$  metal charge transfer in  $\text{PtX}_4^{2-}$  and  $\text{AuX}_4^-$  complexes.<sup>22</sup>

A final observation in favor of the interpretation presented above is that the  $[\text{Pt}(\text{dien})\text{OH}]^+$  complex does not show the band at all in the spectral region examined.

The electronic spectra of several  $[\text{Au}(\text{dien-H})\text{X}]^+$  complexes are given in Table V. The high-energy band in each case is readily assigned to the  $b_2, b_1(\pi^*) \rightarrow 2a_1(\sigma^*)$  transition, since a blue shift is anticipated for  $\text{X} \rightarrow \text{Au}$  type charge transfer in going from  $[\text{Au}(\text{dien})-$

$\text{X}]^{2+}$  to  $[\text{Au}(\text{dien-H})\text{X}]^+$ . The new band, at lower energy, is assigned to the transition  $2p_\pi(\text{dien-H}) \rightarrow 2a_1(\sigma^*)$ , since dien-H has a relatively unstable electron pair in a  $2p_\pi$  type orbital.

The fact that  $[\text{Au}(\text{dien-H})\text{OH}]^+$  shows *only* the low-energy band due to dien-H  $\rightarrow$  Au charge transfer is evidence of the correctness of these assignments.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
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## Polymeric Complexes of Cobalt(III) with Some Mercapto Compounds<sup>1a</sup>

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Hexanethiol (HShex) and cobalt(II) react with oxygen and sodium hydroxide to form a complex  $[\text{Co}(\text{Shex})_3]$ . A product of the same composition also is obtained from (HShex), sodium hydroxide, and *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride. These complexes are very similar to the tris-(3-mercaptopropionato)-cobalt(III) and the triscysteinato-cobalt(III) obtained earlier.<sup>2</sup> It is concluded that these complexes are polymeric and involve only mercaptide-cobalt(III) coordination, with the (Shex) groups acting as bridges between pairs of cobalt(III) atoms (see Fig. 1). Qualitative evidence for the polymeric nature of the complexes is obtained from measurements of viscosity, diffusion, and osmotic pressure. The infrared spectrum of tris-(3-mercaptopropionato)-cobalt(III) indicates that the carboxyl group is not coordinated.

Two triscysteinatocobalt(III) complexes were first prepared by Schubert<sup>3</sup> and further studied by Gorin, *et al.*<sup>2</sup> One complex was obtained at high pH and dissolved in water to give green solutions; the other complex was obtained at lower pH and was very insoluble in water, but could be dissolved in base to give cherry-red solutions. It has been established that nitrogen and sulfur atoms serve as donors in the green complex. The red triscysteinato complex has a visible and ultra-

violet spectrum very similar to that of the complex formed from 3-mercaptopropionic acid, and it seemed reasonable to postulate that these complexes contain chelate rings involving the oxygen and sulfur atoms.<sup>2</sup>

This conclusion could not be regarded as certain, however, and it therefore seemed worthwhile to investigate a ligand containing the mercapto group only. This paper will describe a complex formed from cobalt(III) and hexanethiol (henceforth symbolized by  $[\text{HShex}]$ ) and some of its properties.

### Experimental

**Materials.**—(HShex), obtained from the Eastman Kodak Company, Rochester 3, N. Y., c ystaine hydrochloride hydrate (B

(1) (a) Supported in part by Grant G-5966 from the National Science Foundation. (b) National Science Foundation Cooperative Fellow, 1960–1962; Dow Chemical Corporation Summer Fellow, 1952. (c) To whom inquiries should be sent.

(2) G. Gorin, J. E. Spessard, G. A. Wessler, and J. P. Oliver, *J. Am. Chem. Soc.*, **81**, 3193 (1959).

(3) M. P. Schubert, *ibid.*, **55**, 3336 (1933), and preceding papers.