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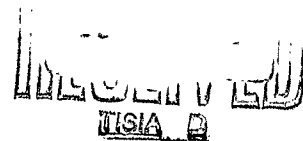
Acidodiethylenetriaminegold(III) Complexes:
Preparation, Solution Chemistry and Electronic Structure

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Abstract

The preparation of acidodiethylenetriaminegold(III) salts with the general formula $[\text{Au}(\text{dien})\text{X}]\text{X}_2$ ($\text{dien} = \text{NH}_2\text{C}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$ and $\text{X} = \text{Cl}^-, \text{Br}^-$) is reported. The complexes are acids in aqueous solution, ionizing a proton from one of the amine nitrogen atoms. The resulting conjugate bases, $[\text{Au}(\text{dien-H})\text{X}]\text{X}^-$ ($\text{dien-H} = \text{dien}$ less one proton and $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$), have been isolated. Equilibrium constants for (N-H) ionization and for the hydrolysis are given. Electronic spectra of the $[\text{Au}(\text{dien})\text{X}]^{2+}$ and $[\text{Au}(\text{dien-H})\text{X}]^{+}$ complexes are assigned using a molecular orbital level classification.

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Introduction

Square planar acidoammine complexes of the type $[M(\text{amine})_nX_{4-n}]^{(n-2)+}$ ($X = \text{Cl}^-$, Br^- , etc.) where $M = \text{Pt}^{2+}$ and Pd^{2+} 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^{3+} .⁵⁻¹²

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This paper reports the general synthesis of complexes of Au^{3+} 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 $[M(\text{dien})X]^{n+}$ ($M = \text{Pd}^{2+}$, Pt^{2+} or Au^{3+}) 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. concentrated HNO₃. The gold dissolved in a minute or so to give an orange solution. This solution was evaporated to 1-2 ml., 5 ml. concentrated HCl was added, and the evaporation repeated. Again, 5 ml. 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 micro-crucible. Using this procedure, determination of gold in two of the compounds, [Au(dien-H)X]X (X = Cl⁻, Br⁻), 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, Illinois.

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^{3+} compounds. This assumption will be implied in the notation that is used throughout this paper. For example, the compound which analyzes as $\text{AuC}_4\text{H}_{13}\text{N}_3\text{Cl}_3$ will be referred to as $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$.

Synthesis of $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ and the Conjugate Base, $[\text{Au}(\text{dien-H})\text{Cl}]\text{Cl}$. 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 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 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 a half-hour. 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 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, 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 HCl was added; the time of addition was 2 hr. The yellow solid was collected on a filter, washed with a small quantity of EtOH, 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. EtOH and a few drops of concentrated 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 $\text{AuC}_4\text{H}_{13}\text{N}_3\text{Cl}_3$: 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. EtOH, 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 HCl was added 0.5 g. of tetrachloroauric acid (1.3 mmole). This solution was cooled to 0°C, 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 $\text{AuC}_4\text{H}_{13}\text{N}_3\text{Cl}_3$: 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 mmole) was dissolved in 6 ml. of water. On adding 4 g. of powdered NaBr (39 mmoles) to the yellow solution, an orange precipitate formed immediately. After cooling in an ice bath for one hour, 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 NaBr, but not quite all of it dissolved. The mixture was filtered, and to the filtrate was added several drops of HClO_4 . Then 60 ml. of 1:1 EtOH:Et₂O 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, EtOH, and anhydrous ether. After drying under vacuum for 3 hr. a yield of 1.2 g. was obtained.

Anal. Calcd. for $\text{AuC}_4\text{H}_{13}\text{N}_3\text{Br}_3$: Au, 36.5%. Found: Au, 36.6%.

The compound was also prepared by treating with NaBr the orange solution formed from the reaction of dien with HAuCl_4 , followed by acidification with HBr. A third procedure used to prepare $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$ was to dissolve HAuCl_4 in HBr, and then add dien at 0°C .

Synthesis of $[\text{Au}(\text{dien-H})\text{Br}]\text{Br}$. To the orange viscous material that resulted from the reaction of HAuCl_4 (prepared from 0.5 g. Au; 2.5 mmoles) with dien (after the ether had been decanted) was added 2.5 g. of powdered NaBr (24 mmoles) and 2 ml. of water. The pH at this point was ca. 9 and 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 HAuCl_4 (prepared from 0.5 g. gold; 2.5 mmoles) and dien was added 5 ml. of water containing 4.2 g. of 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 NaI, yielded a black amorphous solid, the analysis of which was not consistent with the desired product.

Synthesis of $[\text{Au}(\text{dien})\text{Cl}][\text{AuCl}_4]_2 \cdot \text{H}_2\text{O}$. To 5 ml. of water was added 1 g. $\text{dien} \cdot 3\text{HCl}$ (5 mmoles) and 0.5 ml. dien (5 mmoles). This mixture was placed in an ice bath and to it was added 5 ml. of an aqueous solution of 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 HCl, EtOH, and Et_2O . After drying in vacuum for 3 hr., the yield was 0.5 g.

Anal. Calcd. for $\text{Au}_3\text{C}_4\text{H}_{15}\text{N}_3\text{Cl}_9\text{O}$: C, 4.66%; H, 1.47%; Au, 57.31%.
Found: C, 5.77%; H, 1.56%; Au, 57.19%.

Synthesis of $[\text{dienH}_3][\text{AuCl}_4]_3 \cdot \text{H}_2\text{O}$. 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. dien (0.5 mmoles) and 2 ml. of concentrated HCl. The acidified amine solution was added to the 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, EtOH, and anhydrous ether in that order, then air dried for 48 hr.

Anal. Calcd. for $\text{Au}_3\text{C}_4\text{H}_{18}\text{N}_3\text{Cl}_{12}\text{O}$: 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 Bailar¹⁰ was used to prepare $[\text{Au}(\text{en})_2]\text{Cl}_3$. Several other compounds used in this study, $[\text{M}(\text{dien})\text{X}]\text{X}$ ($\text{M}=\text{Pt}^{2+}$, Pd^{2+} ; $\text{X}=\text{Cl}^-$, Br^- , I^-), were previously prepared.¹³

(13) Fred Basolo, Harry B. Gray, and R. G. Pearson, J. Am. Chem. Soc., 82, 4200 (1960).

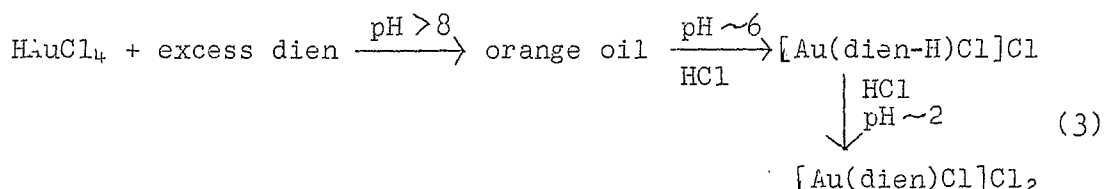
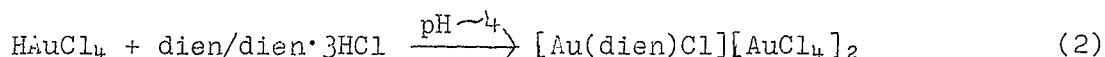
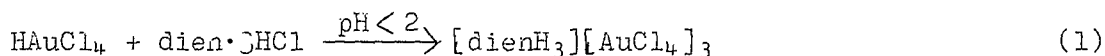
Visible and Ultraviolet Spectra. The visible and UV absorption spectra were measured with Beckman DK-2, Cary 14 and Cary 11 spectrophotometers, using 1 cm. quartz cells. The concentrations, cell compartment temperature, instrument, and reference solutions are listed in the captions to the figures showing the spectra.

Potentiometric Titrations. These were carried out in a jacketed beaker through which water circulated from a constant temperature bath at 25.0 ± 0.1 C. 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. micro-buret 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 CO_2 . The NaOH solutions were prepared with CO_2 -free

water and standardized in duplicate with potassium acid phthalate either immediately before or immediately after the titration was performed. Solutions of 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.

RESULTS AND DISCUSSION

The reaction between 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 equations (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 Pt^{2+} and 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

Table I. potentiometric Titration Data(a)

T = 25°C; Ionic Strength = 0.5

<u>[Complex]x10³ moles/liter</u>	<u>pH_½</u>	<u>pH_{1½}</u>	<u>Salt Added</u>
(A) Titrations of [Au(dien)Cl]Cl ₂			
0.487	3.9	6.2	LiClO ₄
1.209	4.0	6.5	NaClO ₄
2.037	4.0	6.6	NaClO ₄
3.464	4.7	—	NaCl
1.643	4.7	—	NaCl
(B) Titrations of [Au(dien)Br]Br ₂			
1.521	4.6	7.5	NaClO ₄
1.476	4.5	7.5	NaClO ₄
1.517	5.2	—	NaBr
(C) Titrations of [Au(en) ₂]Cl ₃			
1.714	6.3	—	NaClO ₄
2.444	7.2	—	KCl

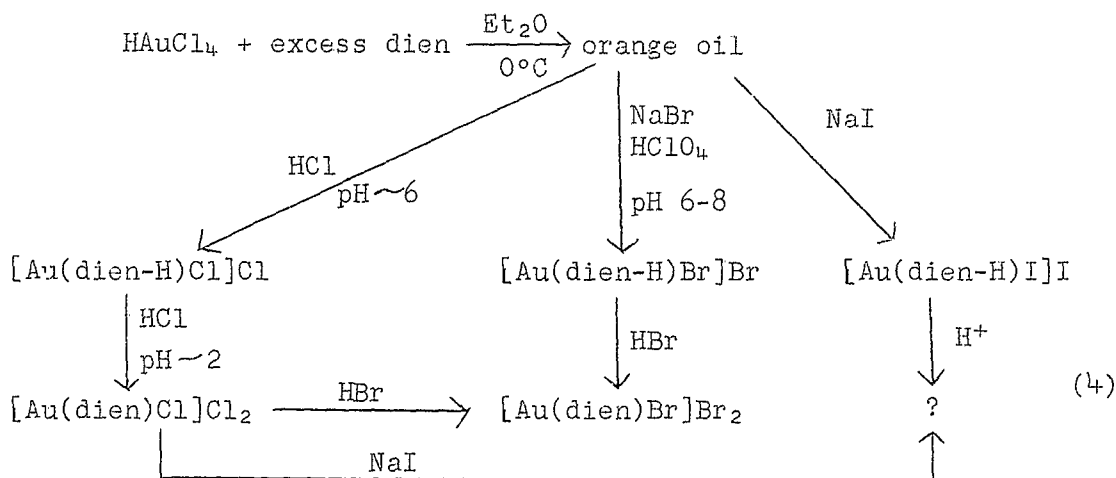
(a) pH_½ is the pH of the solution being titrated when 0.5 moles of OH⁻ per mole complex had been added and pH_{1½} is the pH when 1.5 moles of OH⁻ per mole complex had been added.

reported for Pt^{2+} or Pd^{2+} in aqueous solution,¹⁴ and probably

(14) Amido complexes of Pt^{2+} and 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.

do not exist, but are possible with Au^{3+} due to its larger positive charge. Block and Bailar¹⁰ reported the isolation of the amido complex, $[\text{Au}(\text{en-H})\text{en}]\text{Br}_2$ as well as its conjugate acid.

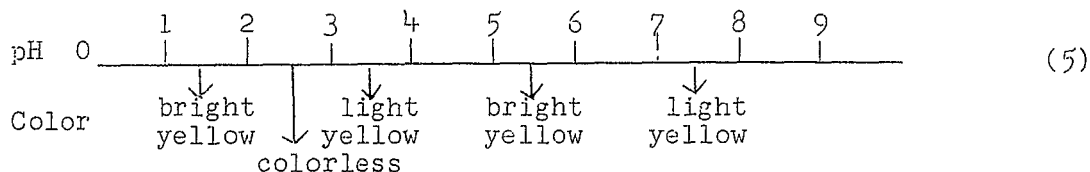
The preparation of amido and amine complexes of Au^{3+} in this investigation is summarized by the reaction scheme (4).



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, $[\text{Au}(\text{dien})\text{X}]\text{X}_2$ ($\text{X}=\text{Cl}^-$, Br^-), appear to be stable indefinitely (no decomposition in a year) in the solid state whereas the amido complexes, $[\text{Au}(\text{dien-H})\text{X}]\text{X}$ ($\text{X}=\text{Cl}^-$, Br^- , 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 $40-50^\circ\text{C}$.

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 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 Au^{3+} , except perhaps in very acidic solution. Bjerrum¹⁵ has noted that aquo species are not present in aqueous

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

solutions of the anionic AuCl_4^- complex.

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 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 Au^{3+} , and the second end point occurring after the addition of exactly two moles of hydroxide ion per mole of 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.¹⁶

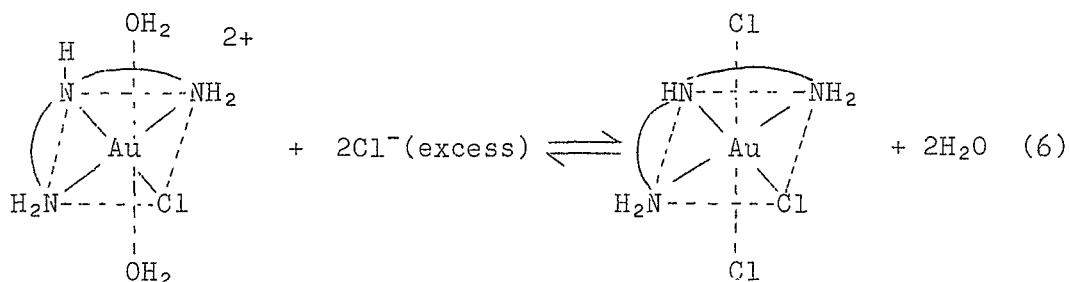
(16) Preliminary kinetic studies of substitution reactions of these complexes show that the covalent halide is completely substituted for in a matter of a few seconds at 25°. Thus, in the course of a potentiometric titration the hydrolysis equilibrium is established very rapidly.

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 $\text{pH}_{1\frac{1}{2}}$ (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 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 $\text{pH}_{1\frac{1}{2}}(\text{Cl})=6.5$ and $\text{pH}_{1\frac{1}{2}}(\text{Br})=7.5$, 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 Figs. 3 and 4. In Fig. 3 one observes that the spectrum of $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ + one equivalent amount of OH^- is different from that of $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$ + one equivalent amount of OH^- . Clearly, the product obtained on adding an equivalent of 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 OH^- to the bromo and chloro complexes, the spectra are identical (Fig. 4). Thus, Fig. 4 is presumably the spectrum of $[\text{Au}(\text{dien-H})\text{OH}]^{1+}$. The spectra in Fig. 4 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 dibasic acid, the spectra of Fig. 4 would be different for $\text{X}=\text{Cl}^-$ and $\text{X}=\text{Br}^-$.

Further insight into the aqueous chemistry of these complexes was obtained by titrating $[\text{Au}(\text{dien})\text{X}]\text{X}_2$ ($\text{X}=\text{Cl}^-$, 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. Fig. 5 shows the titration curve of $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ in the presence of 0.5 M ClO_4^- (Curve A) and in the presence of 0.5 M 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 Au^{3+} . One also observes from Fig. 5 that $\text{pH}_{\frac{1}{2}}$ (that is, pK_a of $[\text{Au}(\text{dien})\text{Cl}]^{2+}$) is 4.0 in 0.5 M ClO_4^- but 4.7 in 0.5 M 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 Cl^- and 0.1 M ClO_4^- are shown in Fig. 6. 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 $[\text{Au}(\text{dien-H})\text{Cl}]^{1+}$. Isosbestic points occur also in the 0.1 M ClO_4^- solutions, but here the isosbestic points are at slightly different wavelengths and the intensities of absorption are different from the solutions containing excess chloride. The isosbestic points in the 0.1 M 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 pK_a values and spectra are due to axial interactions such as shown below by equation (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 of excess anion on the pK_a of Au^{3+} cationic complexes is afforded by the pK_a values of $[\text{Au}(\text{en})_2]^{3+}$ 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

<u>Complex</u>	<u>pK_a(in 0.5 M ClO₄⁻)</u>	<u>pK_a(in 0.5 M X⁻)</u>
[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 ⁻)

(a) The pK_a of [Au(dien)OH]²⁺ was determined by dissolving [Au(dien)Cl]Cl₂ 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](NO₃) was then titrated with HClO₄.

It is interesting to note that the pK_a values of $[\text{Au}(\text{dien})\text{X}]^{2+}$ ($\text{X}=\text{Cl}^-$, Br^- , OH^-) are in the same order of decreasing acidity as was observed for some Pt^{4+} complexes. The pK_a values¹⁷ for

(17) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", John Wiley and Sons, Inc., New York, N. Y., 1958, p. 388.

$[\text{Pt}(\text{NH}_3)_5\text{X}]^{3+}$ were found to be 8.1, 8.3, and 9.5 for $\text{X}=\text{Cl}^-$, Br^- and OH^- , respectively.

The pK_a value of $[\text{Au}(\text{dien})\text{X}]^{2+}$ relative to the pK_a of $[\text{Au}(\text{en})_2]^{3+}$ should be discussed. One might expect $[\text{Au}(\text{en})_2]^{3+}$ with a larger cationic charge to be more acidic than $[\text{Au}(\text{dien})\text{X}]^{2+}$, 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 $[\text{Pt}(\text{NH}_3)_6]^{4+}$ and $[\text{Pt}(\text{NH}_3)_5\text{Cl}]^{3+}$ are 7.9 and 8.1 respectively.¹⁷

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 ¹⁷ of 5.5 for $[\text{Pt}(\text{en})_3]^{4+}$, which is to be compared with a pK_a of 7.9 for $[\text{Pt}(\text{NH}_3)_6]^{4+}$. A chelate effect may be responsible for $[\text{Au}(\text{dien})\text{X}]^{2+}$ being a stronger acid than is

$[\text{Au(en)}_2]^{3+}$. This effect of chelation on acidity has been explained in terms of a decreasing energy of solvation¹⁸ as chelation is

(18) Reference 17, p. 392.

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.¹⁹ Electrostatic effects were divided

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

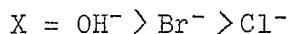
into "inductive effects" which are transmitted through a chain of atoms and "field effects" which are transmitted through empty space or solvent molecules. In the complex $[\text{Au(dien)X}]^{2+}$, transmission of positive charge in the coordinated amine would be via the carbon chain. If one assigns 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 $[\text{Au(dien)X}]^{2+}$ relative to $[\text{Au(en)}_2]^{3+}$. 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 $[\text{Au(dien)X}]^{2+}$. 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 values²⁰ of 4.61 for $dien\ H_3^{3+}$, 9.21 for $dien\ H_2^{2+}$ and 9.98 for

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

$dien\ H^+$. 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



which is the same order as that observed for Pt^{2+} complexes.²¹

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

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

The $[M(dien)X]^{n+}$ complexes ($M=Pd^{2+}$, Pt^{2+} or Au^{3+}) are considered to be square planar, with effectively C_{2v} symmetry. The four ligand atoms (3N's and X) are aligned along the x and y axes, with the x axis taken for C_2 . There are four ligand σ -valence

orbitals (one from each N, one from X) and two π -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 $[M(\text{dien})X]^{n+}$ complexes is shown in Fig. 7. This level scheme was arrived at by modifying the general M.O. scheme²² (D_{4h} symmetry with full

(22) H. B. Gray and C. J. Ballhausen, J. Am. Chem. Soc., 85, 260 (1963).

σ - and π -bonding) for C_{2v} symmetry and limited π -bonding. The ground state of the $[M(\text{dien})X]^{n+}$ 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 $[M(\text{dien})X]^{n+}$ complexes show a single absorption band of intermediate intensity (ϵ range is 200-2000) in the 25,000-40,000 cm^{-1} region. Following the level scheme, the band is assigned $b_2b_1(\pi^*) \longrightarrow 2a_1(\sigma^*)$ [${}^1A_1 \longrightarrow {}^1B_1, {}^1B_2$]. The transition involves transferring an electron from a π -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 $[M(\text{dien})X]^{n+}$ complexes are given in Table IV. For any M, the band increases in energy in the X order

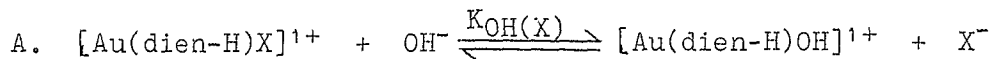
$$I < Br < Cl$$

This is consistent with the assignment of the transition as a

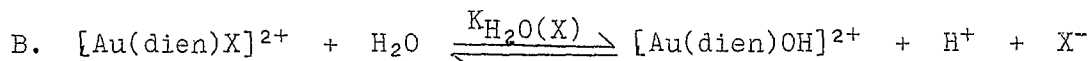
Table III

Hydrolytic Equilibrium Constants

(T = 25°C; μ = 0.5 with ClO_4^-)



X^-	$K_{\text{OH}}(\text{X})^{(a)}$
Cl^-	10^5
Br^-	$10^{4.1}$



X	$K_{\text{H}_2\text{O}}(\text{X})^{(b)}$
Cl^-	6×10^{-8}
Br^-	4×10^{-9}

(a) The values of $K_{\text{OH}}(\text{X})$ were calculated from the expression

$$K_{\text{OH}}(\text{X}) = \frac{\{[\text{Au}(\text{dien-H})\text{OH}]^{1+}\} \{\text{X}^-\}}{\{[\text{Au}(\text{dien-H})\text{X}]^{1+}\} \{\text{OH}^-\}}$$

by assuming that at $\text{pH}_{1\frac{1}{2}}$ in the titration curve (half-way between the first and second end point) the concentration of $[\text{Au}(\text{dien-H})\text{OH}]^{1+}$ equals the concentration of $[\text{Au}(\text{dien-H})\text{X}]^{1+}$. The concentration of X^- at $\text{pH}_{1\frac{1}{2}}$ 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 $\text{pH}_{1\frac{1}{2}}$.

(b) Calculated from the equation

$$K_{\text{H}_2\text{O}}(\text{X}) = K_{\text{a}}(\text{X}) K_{\text{OH}}(\text{X}) K_{\text{w}}/K_{\text{a}}(\text{OH})$$

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

The charge transfer assignment is also indicated from a comparison of analogous Pt^{2+} and Au^{3+} complexes. Thus the band for any given X complex shifts to lower energy in going from Pt^{2+} to the better electron acceptor, Au^{3+} . This type of evidence has been used to assign ligand $\rightarrow$ metal charge transfer in PtX_4^{2-} and AuX_4^- complexes.²²

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

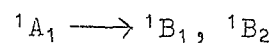
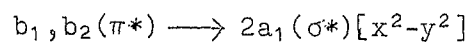
The electronic spectra of several $[Au(dien-H)X]^+$ complexes are given in Table V. The high-energy band in each case is readily assigned to the $b_2, b_1 (\pi^*) \rightarrow 2a_1(o^*)$ transition, since a blue shift is anticipated for $X \rightarrow Au$ type charge transfer in going from $[Au(dien)X]^{2+}$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

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

Acknowledgments. - This research was supported in part by the U.S. Air Force under contract No. AF 49(638)315 and in part by the U.S. Atomic Energy Commission under Contract At(11-1)-1087. One of us (W.H.B.) wishes to thank Northwestern University for a Fellowship during the academic year 1961-1962. Research done at Columbia University was supported by the Petroleum Research Fund of the American Chemical Society.

Table IV

The Long Wavelength Electronic Transition in
 $[M(dien)X]^{n+}$ Complexes



<u>Complex</u>	$\tau(\max) \overset{\circ}{\text{\AA}}$	$\nu_{\max}, \text{cm}^{-1}$	$\epsilon_{\max}$
$[Pd(dien)Cl^+]$	3380	29,590	500
$[Pd(dien)Br^+]$	3450	28,990	450
$[Pd(dien)I^+]$	3700	27,030	500
$[Pt(dien)Cl^+]$	2700	37,040	275
$[Pt(dien)Br^+]$	2750	36,360	250
$[Pt(dien)I^+]$	3000	33,330	500
$[Au(dien)Cl^{2+}]^{(a)}$	3020	33,110	815
$[Au(dien)Br^{2+}]^{(a)}$	3400	29,410	510
$[Au(dien)I^{2+}]^{(b)}$	3830	26,110	1800

(a) Spectrum at pH = 2.5-3.0

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

(a) Equivalent concentrations of $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ and OH^- , with 0.5 M Cl^- .

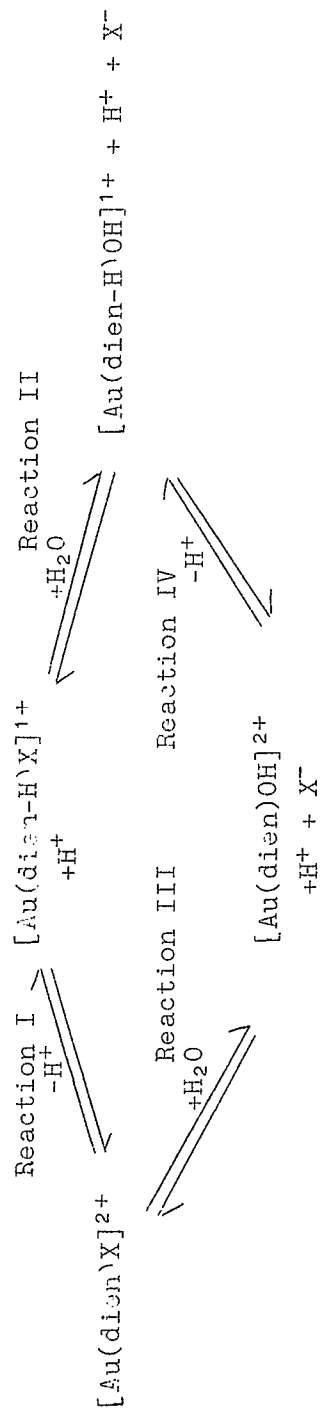
(b) Equivalent concentrations of $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$ and OH^- , with 0.5 M Br^- .

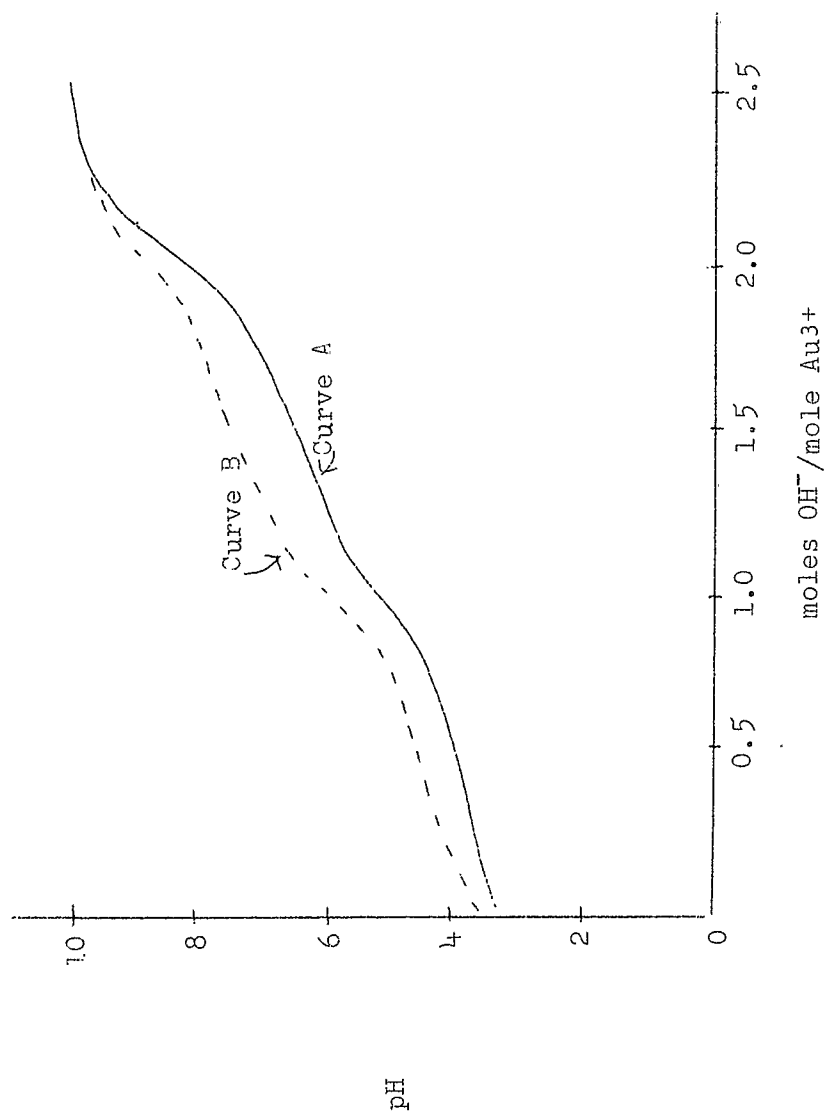
(c) Complex present in a solution originally containing $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ at
pH = 11.5.

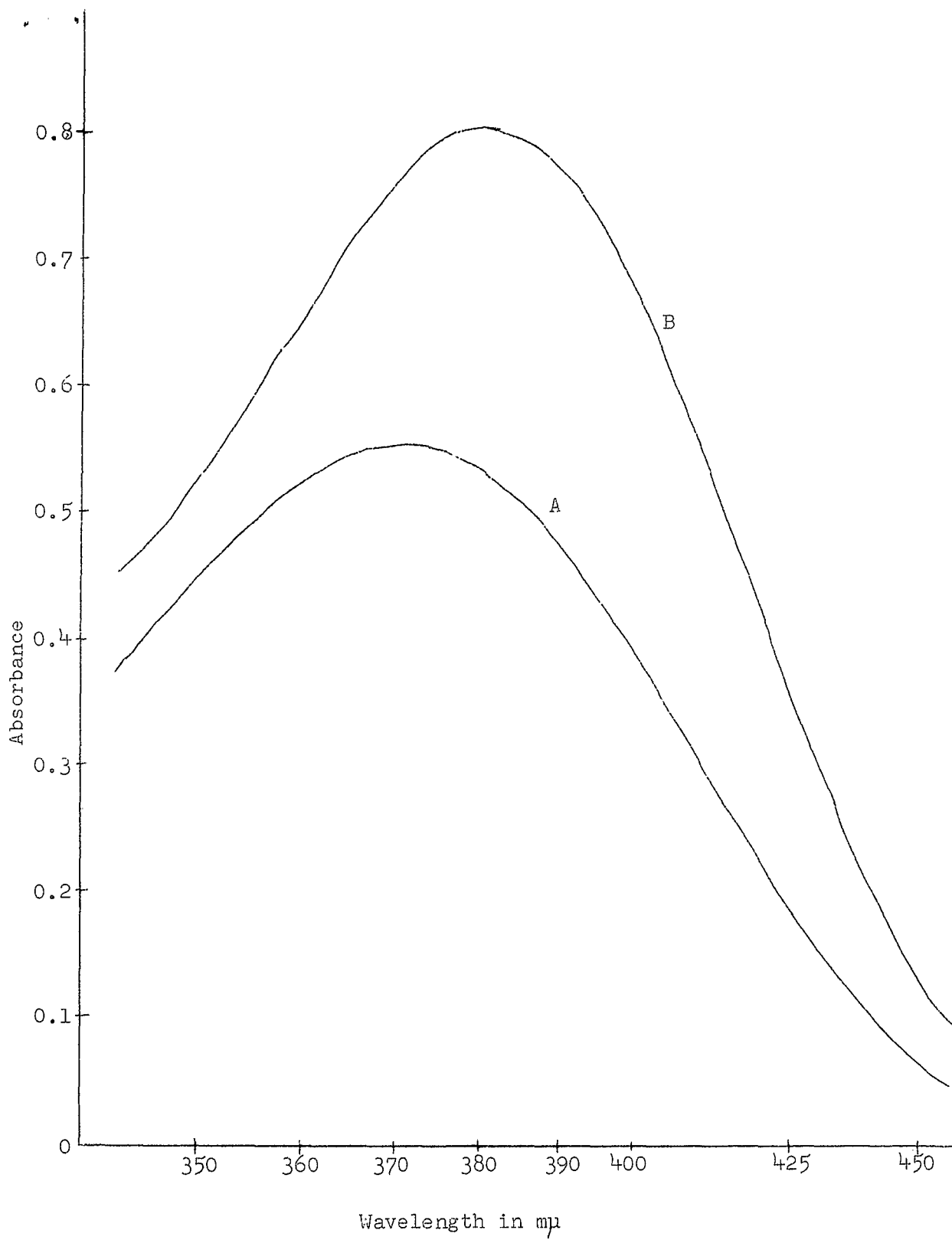
Captions to Figures

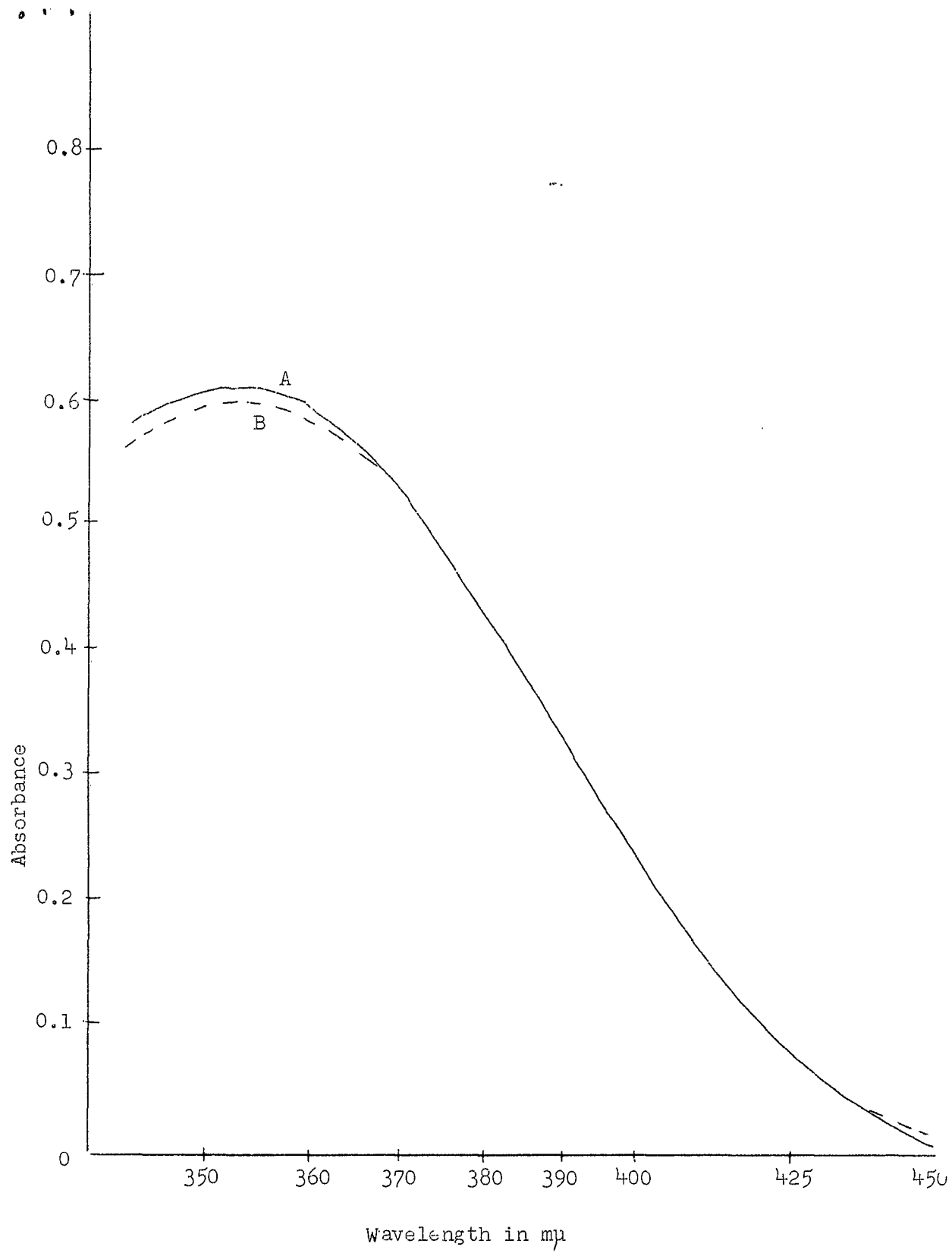
- Fig. 1 - Equilibria occurring in aqueous solutions of $[\text{Au}(\text{dien})\text{X}]\text{X}_2$ ($\text{X}=\text{Cl}^-$, Br^-) in the pH range 2-10.
- Fig. 2 - Curve A: Potentiometric titration curve of 0.1209 mmoles $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ with 0.02433 M NaOH at 24.9°C ; $\mu = 0.5$ with NaClO_4 .
Curve B: Potentiometric titration curve of 0.1476 mmoles $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$ with 0.02433 M NaOH at 24.9°C ; $\mu = 0.5$ with NaClO_4 .
- Fig. 3 - Spectrum A: Absorption spectrum of 3.95×10^{-4} M $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ + one equivalent NaOH.
Spectrum B: Absorption spectrum of 4.01×10^{-4} M $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$ + one equivalent NaOH.
Spectra recorded on Beckman DK-2 Spectrophotometer.
- Fig. 4 - Spectrum A: Absorption spectrum of 3.95×10^{-4} M $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ + two equivalents NaOH.
Spectrum B: Absorption spectrum of 4.01×10^{-4} M $[\text{Au}(\text{dien})\text{Br}]\text{Br}_2$ + two equivalents NaOH.
Spectra recorded on Beckman DK-2 Spectrophotometer.
- Fig. 5 - Curve A: Potentiometric titration of 0.1209 mmoles $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ with 0.02433 M NaOH at 24.9°C ; $\mu = 0.5$ with NaClO_4 .
Curve B: Potentiometric titration of 0.1643 mmoles $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ with 0.08158 M NaOH at 25.0°C ; $\mu = 0.51$ with NaCl.
- Fig. 6 - Absorption spectra of 2.47×10^{-4} M $[\text{Au}(\text{dien})\text{Cl}]\text{Cl}_2$ in the pH range 2.46 - 4.12; ——— in 0.1M NaCl; ----- in 0.1 M LiClO_4 ; pH adjusted with HClO_4 ; pH of solutions - A, 4.12; B, 3.48; C, 2.48; A', 4.00; B', 3.42; C', 2.46.
Spectra recorded on Beckman DK-2 Spectrophotometer.

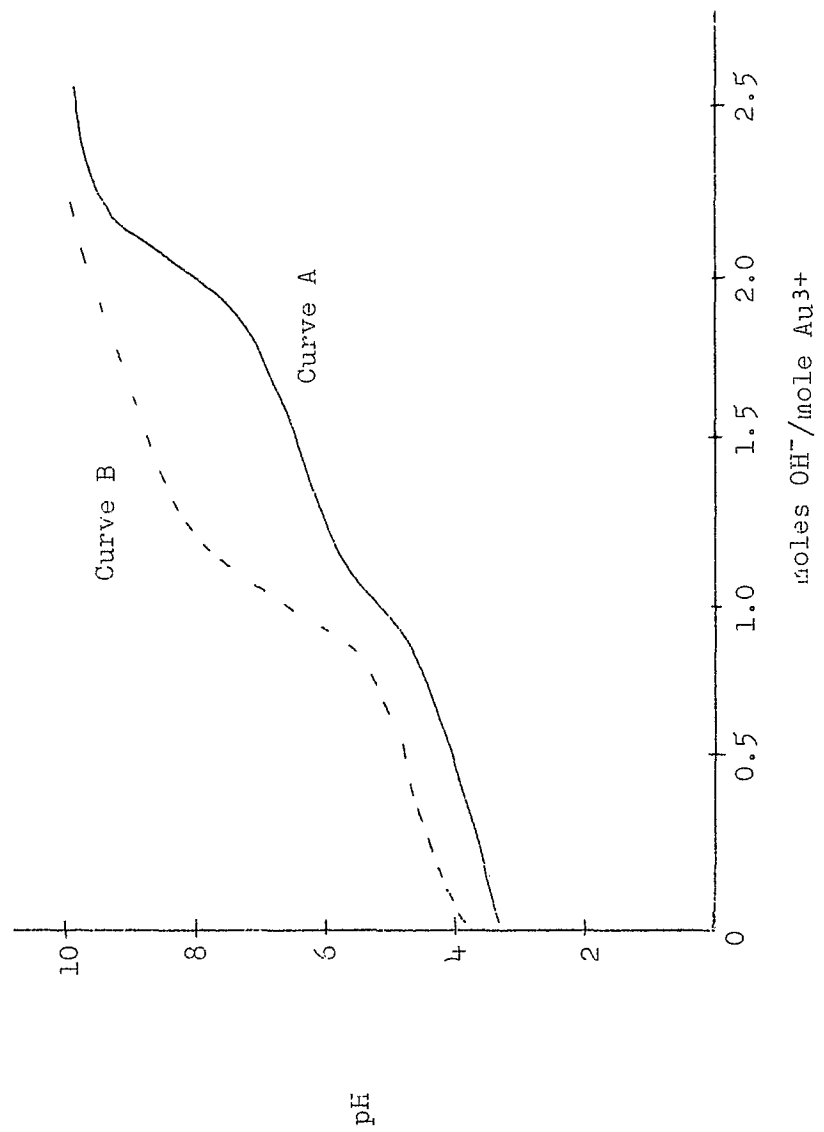
Fig. 7 - Molecular orbital energy level scheme for $[M(\text{dien})X]^{n+}$ complexes.

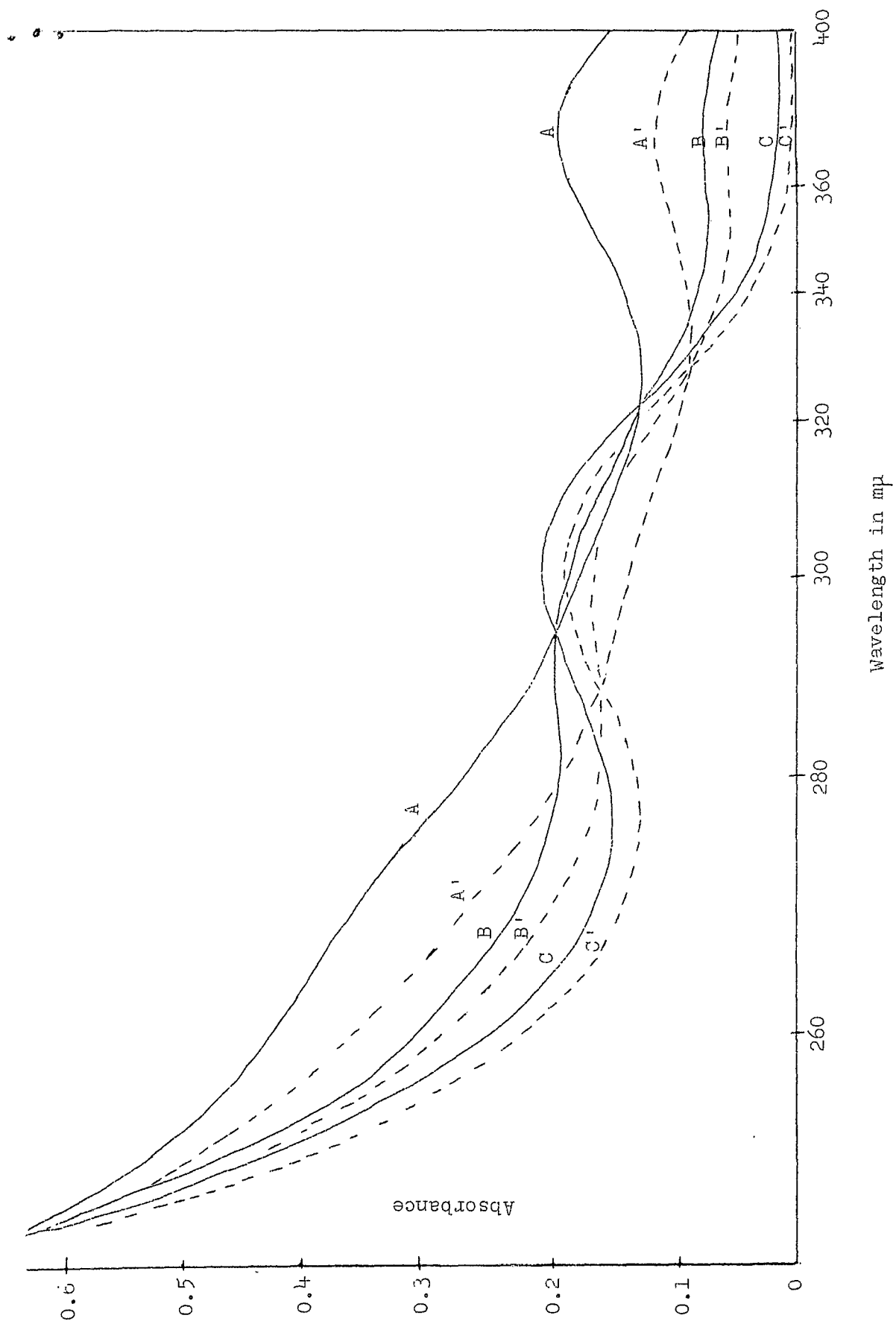








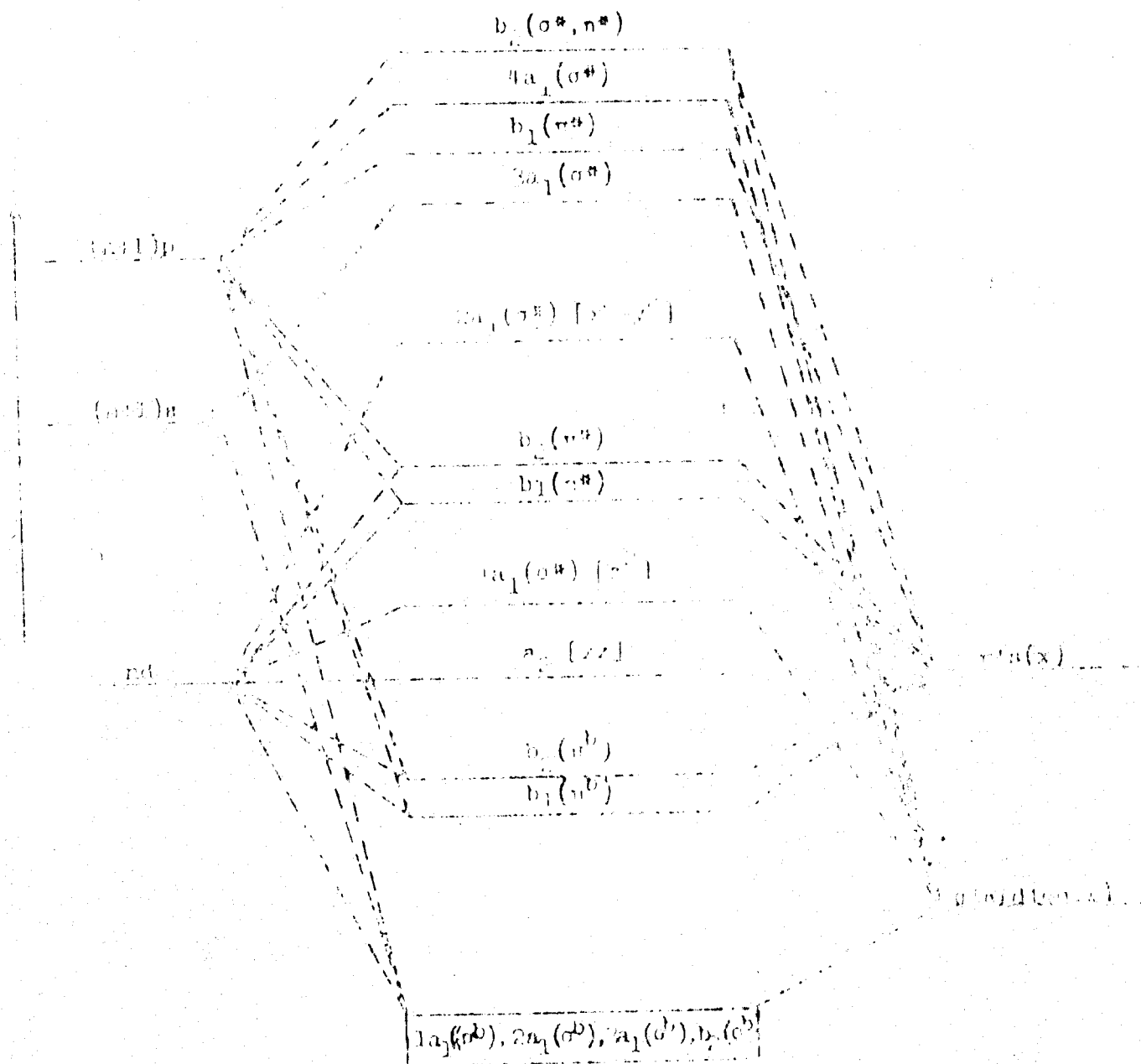




M
orbitals

$M(dien)X^{n+}$
molecular orbitals

dien, X
orbitals



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