

complexed isoquinoline. ^1H nmr (CDCl_3): 4.98 (t, 4, $^2J_{\text{Pt-CH}} = 62$ Hz, ^1H nmr (C_2H_4): 8.75 (m, 1, $^3J_{\text{Pt-NCH}} = 30$ Hz), 9.62 (t, 1, $^3J_{\text{Pt-NCH}} = 41$ Hz). $\nu_{\text{Pt-Cl}}$: 345 cm^{-1} . Dsc: mp 129°; $T_i = 142^\circ$, $T_f = 310^\circ$; % wt loss = 39.9 (obsd), 37.1 (calcd). Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{NPtCl}_2$: C, 31.19; H, 2.62; Pt, 46.10. Found: C, 31.16; H, 2.87; residue, 45.91.

$[\text{C}_9\text{H}_8\text{N}][\text{PtCl}_3(\text{C}_2\text{H}_4)]$, **5**. ^1H nmr (CDCl_3): 4.87 (t, 4, $^2J_{\text{Pt-CH}} = 62$ Hz). $\nu_{\text{Pt-Cl}}$: 338, 309 cm^{-1} . Dsc: mp 120°; $T_i = 129^\circ$, $T_f = 298^\circ$; % wt loss = 41.9 (obsd), 42.1 (calcd). Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{NPtCl}_3$: C, 28.72; H, 2.63; Pt, 42.45. Found: C, 28.80; H, 2.56; residue, 40.60.

trans- $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{iquin})]$, **3**. To 100 mg of *trans*- $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{iquin})]$ dissolved in 5 ml of CHCl_3 was added an equimolar amount of isoquinoline. A yellow precipitate appeared after 6 hr. The solution was allowed to stand for 36 hr and filtered, and the solid product was washed with hexane and dried. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{N}_2\text{Pt}$: C, 41.23; H, 2.69; N, 5.34. Found: C, 39.34; H, 2.72; N, 4.77. $\nu_{\text{Pt-Cl}}$: 338 cm^{-1} and a peak at 294 cm^{-1} which has yet to be unequivocally assigned. Dsc: $T_i = 298^\circ$, $T_f = 337^\circ$, % wt loss = 46.3 (obsd), 49.2 (calcd). This compound has been prepared previously⁸ by irradiation of *cis*- $[\text{PtCl}_2(\text{iquin})_2]$ but was not isolated. The analogous pyridine complex has been prepared by a similar method.⁹

1,3-Bis(isoquinoline)- μ -dichloro-2,4-dichlorodiplatinum(II), **4**. A solution of 432 mg (1 mmol) of *trans*- $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{iquin})]$ in 20 ml of CHCl_3 was irradiated (500-W Hg lamp) in a Pyrex vessel for 48 hr. The orange-yellow precipitate was filtered, washed with hexane, and dried. The solid consisted of two compounds, the less soluble **2** (in CHCl_3), *cis*- $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{iquin})]$, and the more soluble, previously unreported $[\text{Pt}_2\text{Cl}_4(\text{iquin})_2]$. Anal. Calcd for *cis*- $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{iquin})]$, $\text{C}_{11}\text{H}_{11}\text{NPtCl}_2$: C, 31.19; H, 2.62; N, 3.36. Found: C, 31.18; H, 2.61; N, 3.38. $\nu_{\text{Pt-Cl}}$: 344, 310 cm^{-1} . ^1H nmr (CDCl_3) (3200 spectra were time-averaged because of the low solubility in CDCl_3): 4.83 (t, 4, $^2J_{\text{Pt-CH}} = 62$ Hz (C_2H_4)), 8.80 (m, 1, $^3J_{\text{H-H}} = 6$ Hz, $^3J_{\text{Pt-NCH}} = 31$ Hz), 9.81 (t, 1, $^3J_{\text{Pt-NCH}} = 39$ Hz). Dsc: $T_i = 155^\circ$, $T_f = 338^\circ$; % wt loss = 37.9 (obsd), 37.1 (calcd).

1,3-Bis(isoquinoline)- μ -dichloro-2,4-dichlorodiplatinum(II). Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{Pt}_2\text{Cl}_4$: C, 27.34; H, 1.79; Cl, 17.96. Found: C, 27.19; H, 1.82; Cl, 18.19. $\nu_{\text{Pt-Cl}}$: 351, 324 cm^{-1} .

The corresponding piperidine dimer was isolated¹⁰ from an aged (2 months) petroleum ether solution of *trans*- $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{piperidine})]$ but it is not clear whether this was just a slow reaction or was the result of inadvertent irradiation.

cis- $[\text{PtCl}_2(\text{iquin})_2]$. To a solution of 100 mg of *cis*- $[\text{PtCl}_2$

(C_2H_4)(*iquin*)] in 50 ml of CHCl_3 was added an equimolar amount of isoquinoline. The solution was allowed to stand for 48 hr and evaporated to dryness. The solid *cis*- $[\text{PtCl}_2(\text{iquin})_2]$ was washed with hexane and dried. This complex was also prepared by cleavage of the isoquinoline dimer with isoquinoline. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{PtCl}_2$: C, 41.23; H, 2.69; N, 5.24. Found: C, 41.17; H, 2.80; N, 5.09. $\nu_{\text{Pt-Cl}}$: 338, 330 cm^{-1} . Dsc: $T_i = 229^\circ$, $T_f = 302^\circ$; % wt loss = 46.3 (obsd), 51.7 (calcd). This complex has been previously prepared by treatment of K_2PtCl_4 with isoquinoline.⁸

Precipitation of *trans*- $[\text{PtCl}_2(\text{iquin})_2]$ from Solution of **1**. A freshly prepared 1 M CDCl_3 solution of **1** (no $^3J_{\text{Pt-NCH}}$) was allowed to stand in the dark for 1 day after which $^3J_{\text{Pt-NCH}}$ was observed. To 1 ml of this solution was added 12 μl (10 mol %) of isoquinoline. After 24 hr a yellow-white precipitate appeared which was separated from the supernatant by centrifugation. The solid precipitate was washed with 5 ml of cold hexane and dried *in vacuo*. The ir spectrum and a dsc analysis showed it to be *trans*- $[\text{PtCl}_2(\text{iquin})_2]$ containing a small amount of **1**. The supernatant solution, after standing in the dark for 1 additional day, showed $^3J_{\text{Pt-NCH}}$.

Acknowledgment. We wish to thank Engelhard Industries, Inc., for a generous supply of platinum, the Atlantic Richfield Corp., for a fellowship to F.P., Dr. L. Spaulding for some of the experimental work, Mr. R. Nowak for the ^1H nmr CAT spectra, and Professor Daryl H. Busch for fruitful discussions about ligand-exchange phenomena.

Registry No. **1**, 51020-82-7; **2**, 50936-84-0; **3**, 26026-48-2; **4**, 54120-17-1; **5**, 54120-18-2; $[\text{PtCl}_3(\text{C}_2\text{H}_4)]$, 12012-50-9; *cis*- $[\text{PtCl}_2(\text{iquin})_2]$, 54163-76-7.

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Cis and Trans Elimination in the Reduction of *cis*-Dichlorobis(propylenediamine)platinum(IV) Ion

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Reduction of *cis*- $[\text{Pt}(\text{pn})_2\text{Cl}_2]^{2+}$ by Eu^{2+} in acidic aqueous solution results in the immediate release of two chloride ions with the formation of $\text{Pt}(\text{pn})_2^{2+}$. Reduction by Cr^{2+} produces no ionic chloride. The products are $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, and a chloride-containing platinum(II) complex presumed to be $\text{Pt}(\text{pn})(\text{pnH})\text{Cl}^{2+}$ with a monodentate propylenediamine ligand. The results are interpreted in terms of an inner-sphere two-electron reduction of Pt(IV) by Cr^{2+} with trans elimination of ligands, in contrast with one-electron reductions by Eu^{2+} with cis elimination.

Introduction

The mechanisms of oxidative addition and reductive elimination reactions are not well understood.¹ In the interconversion of four-coordinate d^8 Pt(II) and six-coordinate d^6 Pt(IV), trans addition and elimination are generally observed, but there have been few examples in which cis addition or elimination is likely. In the present study we have investigated the reduction of *cis*-dichlorobis(propylenediamine)platinum(IV) ion to determine whether cis elimination

occurs to give the thermodynamically stable $\text{Pt}(\text{pn})_2^{2+}$ product (A) or whether trans elimination occurs to give a metastable species with a monodentate propylenediamine ligand (B). Two different reducing agents were used, to examine any differences between the probable one-electron reduction by Eu^{2+} and the possible two-electron reduction by Cr^{2+} .

Experimental Section

Preparation of Complexes. *cis*-Dichlorobis(propylenediamine)platinum(IV) Chloride. The preparation of *cis*- $[\text{Pt}(\text{pn})_2\text{Cl}_2]\text{Cl}_2$

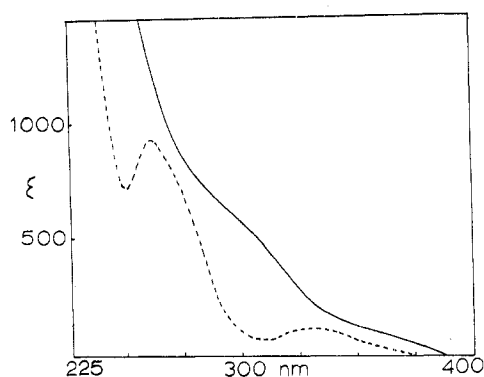
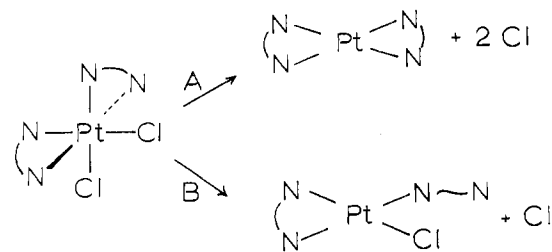


Figure 1. Electronic absorption spectra of *cis*-[Pt(pn)₂Cl₂]Cl₂ (—) and *trans*-[Pt(pn)₂Cl₂]Cl₂ (····) in aqueous solution.



followed the general procedure of Grinberg and Vrublevskaia.² Since their synthesis is not generally available, full details will be given. To a suspension of 9.0 g (22 mmol) of Pt(pn)Cl₄ in 250 ml of water was added a stoichiometric amount of propylenediamine (19 ml of 10% v/v, 22 mmol). The suspension was heated with stirring on a steam bath until complete dissolution had occurred (approximately 45 min). After 15 min additional heating, 30 ml of 10 M HCl was added and the solution was evaporated to near dryness, yielding a yellow-brown residue. This residue was stirred with successive 50-ml portions of cold 0.1 M HCl until the supernatant solution was no longer red but straw yellow. The residue which remained was found to be predominantly the starting material, Pt(pn)Cl₄, and was used in subsequent syntheses. (If the concentrated HCl were not added before the initial evaporation step, but the isolation procedure continued as described above, the residue was predominantly Pt(pn)Cl₂.)

The combined HCl extracts were reduced in volume to 20 ml. After cooling and standing of the mixture for several hours the off-white precipitate which formed was collected by filtration and 40 ml of alcohol was added to the filtrate. The further crop of off-white powder which formed was also collected and the filtrate was reduced in volume to about 5 ml. Further addition of alcohol produced more crude product for a combined yield of 0.8 g. The combined product was dissolved in 30 ml of 0.1 M HCl, the solution filtered, and the filtrate evaporated to 5 ml on a steam bath. After cooling and standing of the mixture for several hours, the snow-white precipitate was collected by filtration. Addition of alcohol to the filtrate produced more snow white product for a combined yield of 0.52 g (4%). *Anal.* Calcd for C₆H₂₀N₄Cl₄Pt: C, 14.9; H, 4.1; N, 11.5; Cl, 29.3; Pt, 40.2. Found: C, 15.2; H, 4.1; N, 11.2; Cl, 28.4; Pt, 39.8.

The complex was further characterized by titration with silver nitrate, which verified the formulation of two ionic chlorides per platinum, by its electronic absorption spectrum, which differs from that of the isomeric *trans* complex (Figure 1), and by its infrared spectrum, which is more complex than that of the *trans* isomer in the region 600–250 cm⁻¹.

Tetrachloropropylenediamineplatinum(IV) and *trans*-Dichlorobis(propylenediamine)platinum(IV) Chloride. These complexes were prepared by Werner's methods of bubbling chlorine through suspensions of Pt(pn)Cl₂ and solutions of [Pt(pn)₂]Cl₂, respectively.³

Dichloropropylenediamineplatinum(II). The preparation described by Dwyer and Sargeson,⁴ using stoichiometric proportions of propylenediamine and K₂PtCl₄, was unsuccessful, but a modified procedure using an excess of propylenediamine gave the desired product. In a typical preparation, 12.3 g of finely powdered K₂PtCl₄ was added rapidly with stirring to a threefold excess of propylenediamine (7.0 ml) in 14 ml of 10 M HCl and 200 ml of 5 M sodium acetate solution. The solution was cooled in an ice bath and 8.5 g of Pt(pn)Cl₂ collected by filtration.

Preparation of Solutions. *cis*-[Pt(pn)₂Cl₂](ClO₄)₂ solutions were prepared by dissolving a weighed quantity of *cis*-[Pt(pn)₂Cl₂]Cl₂ in 0.5 M HClO₄ and titrating with AgClO₄ solution prepared by dissolving Ag₂CO₃ in HClO₄. The titration was stopped at the end point corresponding to the precipitation of the two ionic chlorides, the solution was warmed to coagulate the silver chloride precipitate and centrifuged, the supernatant solution was removed, and the residue was washed. The combined solution and washings were then diluted to a known volume.

Europium(II) Solutions. A standard 1.0 × 10⁻² M europium(III) trifluoroacetate solution was prepared by dissolving europium(III) oxide (Research Organic/Inorganic Chemical Corp., 99.9%) in excess trifluoroacetic acid. A portion of this solution was then reduced over freshly prepared zinc amalgam under an atmosphere of nitrogen. Europium(II) perchlorate solutions were prepared similarly using perchloric acid.

Chromium(II) Trifluoromethylsulfonate Solutions. Crushed chromium metal (United Mineral and Chemical Corp., 99.9%) was immersed in 1 M trifluoromethylsulfonic acid and the mixture deoxygenated in a serum bottle by bubbling nitrogen. A small chip of chromium metal was then activated in concentrated HCl, washed with 1 M trifluoromethylsulfonic acid, and transferred to the serum bottle. The chromium metal dissolved to yield a sky blue solution. Chromium(II) perchlorate solutions could not be prepared in this manner without contamination from a trace of chloride ion apparently formed by the reduction of perchlorate ion in the dissolution process.

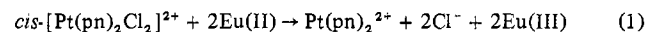
Analytical Methods. Chromium(III) products were separated on a Dowex 50W-X8 100–200 mesh cation-exchange column purified by stirring with 5 M trifluoroacetic acid. The chromium content of the eluted species was determined spectrophotometrically as chromate following alkaline oxidation with hydrogen peroxide. It was found that this procedure resulted in loss of chloride, so chloride analysis of the eluted fractions was performed by hydrolyzing the complex in basic solution for several hours, acidifying and warming for several hours, and then titrating with standard silver nitrate solution. The chromium content of species retained on the resin after elution with 5 M HClO₄ was determined spectrophotometrically as chromate after oxidizing a suspension of the resin with alkaline peroxide. A similar treatment was used to remove platinum species retained on portions of the resin. The platinum was then detected qualitatively using a colorimetric test with stannous chloride.⁵

All titrations and pH-Stat experiments were performed automatically using a Radiometer TTT2 titrator and associated equipment.

Results

Reduction of *cis*-[Pt(pn)₂Cl₂]²⁺ with Eu²⁺. A deoxygenated solution of 5.0 × 10⁻⁴ M *cis*-[Pt(pn)₂Cl₂](ClO₄)₂ in 0.33 M HClO₄ was reduced with a stoichiometric amount of europium(II) perchlorate solution. The product solution was titrated with standard silver nitrate solution and an end point equivalent to two chloride ions per platinum observed. Similarly, reduction of a solution of 5.0 × 10⁻³ M *cis*-[Pt(pn)₂Cl₂]Cl₂ in 0.1 M trifluoroacetic acid with a stoichiometric amount of europium(II) trifluoroacetate solution produced a product solution containing four chloride ions per platinum.

These results indicate the stoichiometry of the reduction reaction to be



To confirm the absence of a possible protonated open chelate ligand in the platinum(II) product, a very slow pH titration was performed. An aliquot of the platinum(II) product solution was quickly adjusted to pH 3 and then titrated with 10⁻² M NaOH solution to pH 10 over a 10-hr period. A similar experiment was performed using a solution prepared in an identical manner except that, instead of platinum(IV), air was used to oxidize the europium(II). No difference was observed in the titration curves of the two solutions. Both were buffered in the region pH 5–6, but the amount of base required in the titration could be attributed to the europium(III) and zinc(II) ions present. There is thus no evidence for the titration of a protonated ligand on the platinum(II) product.

Reduction of *cis*-[Pt(pn)₂Cl₂]²⁺ by Cr²⁺. Reduction with

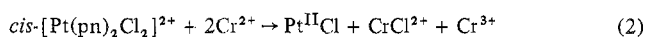
excess aquochromium(II) ion was achieved by adding a deoxygenated solution of $3 \times 10^{-3} M$ *cis*-[Pt(pn)₂Cl₂](ClO₄)₂ in 0.5 M HClO₄ to a solution of $5 \times 10^{-2} M$ chromium(II) in 0.5 M trifluoromethylsulfonic acid. Aliquots of the resulting product solutions after air oxidation of the excess chromium(II) were then analyzed in three different types of experiments.

1. Ion-Exchange Chromatography. Elution of the product solution on a cation-exchange column revealed three chromium species. One of these was identified as Cr(H₂O)₅Cl²⁺ by its green color, by its rapid elution with 2 M HClO₄, and by the titration of an equivalent amount of chloride ion following base hydrolysis of the eluted fraction. A second species was identified as Cr(H₂O)₆³⁺ by its violet color, by its rapid elution with 5 M HClO₄, and by the absence of chloride ion following attempted base hydrolysis. The third species is presumed to be polymeric chromium(III) from its blue-violet color and the failure to elute it with strong acid.

Assuming the expected stoichiometry of 2:1 Cr(II):Pt(IV), the polymeric chromium(III) product corresponds to the amount of excess chromium(II) oxidized by air after completion of the platinum reduction. The CrCl²⁺ and Cr³⁺ formed by reduction of the platinum(IV) were found in equivalent amounts.

Qualitative analysis of the lower half of the ion-exchange column revealed a platinum-containing species retained on the column after elution with 5 M HClO₄. Quantitative titration of the solution obtained by alkaline peroxide oxidation of this portion of the column indicated the presence of eight-tenths of a chloride ion per platinum reduced. Since some loss of chloride during heating with peroxide was observed in blank experiments, a value less than 1.0 is expected.

2. Titration of Ionic Chloride. Titration of the acidic product solution with standard silver nitrate solution indicated the absence of chloride ions. However, titration of an aliquot of the product solution which had been hydrolyzed at pH 4.2 for 40 hr indicated the presence of one chloride ion per platinum reduced. Titration of an aliquot of the product solution which had been hydrolyzed at pH 5.2 for 60 hr indicated the presence of two chloride ions per platinum. These results, together with the chromatographic separation of the product solution, indicate the stoichiometry of the reduction to be



3. Controlled-pH Hydrolysis. An aliquot of the product solution was maintained at pH 4.2 by addition of NaOH solution using an automatic titrator operating in the pH-Stat mode. Addition of approximately one OH⁻ per platinum occurred in a first-order process with a half-life of 2–3 hr. After 40 hr the solution was acidified and a portion analyzed for ionic chloride. As indicated above, one chloride ion per platinum was found. The remaining solution was chromatographed on an ion-exchange column. No CrCl²⁺ was observed, but two Cr³⁺ per platinum were eluted with 5 M HClO₄.

In a related experiment the appearance of ionic chloride was observed potentiometrically at pH 2.5. The process was first order with a half-life of 20–25 hr.

These results are interpreted as evidence of the pH-dependent base hydrolysis of CrCl²⁺, which at pH 4.2 is accompanied by ionization of the Cr³⁺ product.

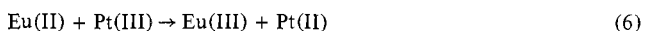
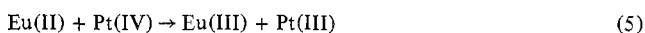


Further hydrolysis of the product solution was observed at pH 5.2. An aliquot of the acidic product solution was adjusted to pH 5.2 by addition of NaOH solution over a 10–15-min period. This time is sufficient for hydrolysis of CrCl²⁺ to proceed to completion. The pH was then maintained at 5.2

by automatic addition of base. Over 60 hr addition of 1 mol of base per platinum was observed with a half-life of approximately 7–8 hr. After acidifying, titration with AgNO₃ indicated the presence of two chloride ions per platinum complex.

Discussion

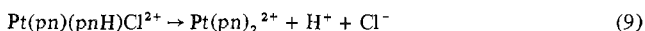
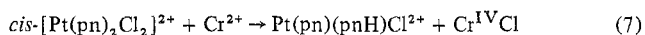
Reduction of *cis*-[Pt(pn)₂Cl₂]²⁺ with Eu²⁺ in acidic aqueous solution results in the release of the two chloride ions originally coordinated in the platinum(IV) complex. The platinum(II) product is apparently the thermodynamically stable bis-(propylenediamine)platinum(II) ion, since there is no evidence from the pH titration curve of the product solution for a titratable proton associated with a monodentate propylenediamine ligand. Previous work⁶ and the present results in the reduction by Cr²⁺ indicate that such an open chelate complex can be trapped in solution of low pH. The stoichiometry of the reduction is therefore that given in eq 1. Since Eu²⁺ is assumed to be limited to one-electron reductions, the mechanism presumably involves a Pt(III) intermediate.



Overall the reduction results in *cis* elimination of two chloride ions from the platinum complex, but there is no evidence at which stage in the reaction this occurs. The Pt(III) coordination sphere may be sufficiently nonrigid to permit the necessary reorganization of the propylenediamine ligands from *cis* octahedral to square planar, or this rearrangement may occur as the Pt(II) complex is generated.

Reduction with Cr²⁺ proceeds with a different stoichiometry. No chloride ions are found in the initial product solution. One chloride is found coordinated to one of the chromium(III) products, suggesting a probable inner-sphere reduction mechanism. The other chloride ion is associated on a cation-exchange column with the platinum(II) product. Upon base hydrolysis at pH 5.2 this chloride is released, together with one proton.

A mechanism consistent with these observations involves *trans* elimination from the platinum(IV) complex in an inner-sphere two-electron reduction by Cr²⁺. This produces a square-planar platinum(II) product with a coordinated chloride and one monodentate protonated propylenediamine ligand. At higher pH ring closure occurs with displacement of the coordinated chloride and release of a proton.



Previous work in our laboratories has furnished precedents for reactions 8 and 9. The reduction of Pt(NH₃)₅Cl³⁺ by Cr²⁺ was interpreted with a mechanism involving reaction 8.⁷ A ring-closure reaction analogous to (9) but with ethylenediamine as the ligand was found to proceed with a roughly comparable rate.⁶ Thus, although alternative one-electron reduction mechanisms cannot be excluded, the transfer of only one chloride ligand to the chromium reducing agent and the appearance of the ring-open platinum(II) product strongly support a one-step two-electron reduction of Pt(IV) to Pt(II) by Cr²⁺ with *trans* elimination of the Pt(IV) ligands. This contrasts with the stereochemical rearrangement which accompanies the two-step one-electron reductions by Eu²⁺.

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Registry No. *trans*-[Pt(pn)₂Cl₂]Cl₂, 54192-98-2; *cis*-[Pt(pn)₂Cl₂]²⁺, 54192-99-3; Pt(pn)Cl₂, 33727-98-9; Eu²⁺, 16910-54-6; Cr²⁺, 22541-79-3.

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Circular Dichroism of Copper(II) β -Diketonates in Optically Active Bases

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The absorption and circular dichroism (CD) spectra of five copper(II) β -diketonate complexes, dissolved in optically active α -phenylethylamine and nicotine, were measured in the visible and near-ultraviolet regions. The profiles of the absorption spectra in the d-d region suggested the coordination of the bases to the axial position of the copper(II) complexes. The main CD band in the d-d region was observed at the lower wave number side within the d-d absorption band, and it may correspond to the magnetic dipole allowed d-d transition which is directed to the z axis in the complex. A considerably intense CD band was also observed in the π - π^* transition region of the β -diketonate ion. The anisotropy factor ($\Delta\epsilon/\epsilon$) of the π - π^* band decreased abruptly with increase of the band separation from the lowest energy band of the optically active amine.

In the course of the investigations on the axial coordination in copper(II) complexes, we have studied the circular dichroism of the copper(II) complexes with optically active ligands.¹ In this study, we wish to report on the CD spectra of some copper(II) β -diketonate complexes in optically active bases.

It is well known that the d-d absorption spectra of copper(II) β -diketonates are much influenced by the variation of solvents and that the positions and intensities of the spectra depend primarily upon the solvent basicity.^{2,3} The stronger ligation to the copper(II) ion along the tetragonal axis causes an appreciable shift of the d-d absorption band to lower energy and results in an increase of the intensity of the band.

Bosnich has reported that when the complex Na₂[PtCl₄] is dissolved in *l*-2,3-butanediol, a CD band appears at only one magnetic dipole allowed d-d transition which is directed to the z axis and suggested that the dissymmetric influences of the optically active solvent are concentrated and directed to the tetragonal positions of the complex ion.⁴

In the cases of the copper(II) β -diketonates dissolved in optically active bases, it is expected that the dissymmetric influences of the solvent upon the complexes are along the tetragonal axis and that, according to the suggestion of Bosnich,⁴ optical activity is observed at only the magnetic dipole allowed d-d transition which is directed to the z axis. In this paper, this expectation was qualitatively supported by the CD measurements.

Experimental Section

Materials. Four copper(II) β -diketonate complexes, *i.e.*, bis(acetylacetonato)copper(II) (abbreviated to Cu(acac)₂), bis(benzoylacetonato)copper(II) (Cu(bzac)₂), bis(dibenzoylmethanato)copper(II) (Cu(dbm)₂), and bis(dipivaloylmethanato)copper(II) (Cu(dpm)₂),⁵ were prepared according to the method described in the literature.⁶ Cu(acac)₂ and Cu(bzac)₂ from methanol, Cu(dbm)₂ from dioxane-water, and Cu(dpm)₂ from ethanol were recrystallized, respectively. Bis(diisobutyrylmethanato)copper(II) (Cu(dibm)₂) was supplied by Dr. Hiroshi Yokoi in this institute.

As optically active bases *d*- or *l*- α -phenylethylamine and 1-methyl-2-(3-pyridyl)pyrrolidine (nicotine) were used. The phenylethylamine was resolved according to the literature method.⁷ The values of the specific rotatory power, $[\alpha]_D$, were +36.0° for the *d* antipode of the amine at 25° and -40.8° for the *l* antipode at 20°. The nicotine was obtained commercially and used after the reduced pressure distillation. The value of $[\alpha]_D$ was -155° at 25°.

Measurements. The five copper(II) β -diketonate complexes were

Table I. Numerical Data for Absorption and CD Spectra in the Optically Active Bases^a

Complex	Solvent base	Absorption ν_{\max} (ϵ)	CD ν_{\max} ($\Delta\epsilon$)
Cu(acac) ₂	<i>d</i> - α -Phenylethylamine	14.6 (78)	12.9 (+0.04 ₂)
		26 sh (260)	25.3 (-0.06 ₂)
		32.6 (25,000)	32.5 (-21)
	Nicotine	15.3 (75)	13.5 (-0.02 ₂)
Cu(bzac) ₂	<i>d</i> - α -Phenylethylamine	26 sh (400)	26.3 (-0.02)
		14.4 (92)	13.1 (+0.05 ₄)
		30.3 (28,500)	30.3 (-3.1)
	Nicotine	15.2 (90)	13.1 (-0.00 ₇)
Cu(dbm) ₂	<i>d</i> - α -Phenylethylamine	15.8 (+0.00 ₂)	15.8 (+0.00 ₂)
		14.4 (103)	13.2 (+0.05 ₈)
		28.0 (41,000)	27.7 (-2.0)
	Nicotine	15.0 (92)	14.2 (+0.01 ₄)
Cu(dpm) ₂	<i>d</i> - α -Phenylethylamine	14.6 (106)	13.6 (-0.09)
		25.5 sh (160)	17.8 (+0.01 ₄)
		33 sh (10,000)	22.8 (+0.01)
	Nicotine	25.7 (-0.05 ₂)	25.7 (-0.05 ₂)
Cu(dibm) ₂	<i>l</i> - α -Phenylethylamine	34.0 (+1.0)	34.0 (+1.0)
		14.4 (96)	12.8 (-0.02 ₄)
		25 sh (180)	16.5 (-0.01 ₁)
	Nicotine	33.5 sh (20,000)	25.6 (+0.10)
		28.5 (+0.14)	28.5 (+0.14)
			34.5 (-2.0)

^a In 10³ cm⁻¹; sh = shoulder.

dissolved in the optically active bases, and the absorption and CD spectra were measured at room temperature. The absorption spectra were obtained by means of a Hitachi EPS-3T spectrophotometer, and the CD measurements in the region from 270 to 1000 nm were made on a JASCO J-20A spectropolarimeter. All molar absorptivities, ϵ , and differential molar absorptivities, $\Delta\epsilon$, between left and right circularly polarized lights refer to 1 mol of copper(II) ion.

The CD spectra in the ligand-field region of Cu(acac)₂ and Cu(bzac)₂ in *d*- α -phenylethylamine exhibited remarkable change with time, while the absorption spectra were little affected. All spectra were measured immediately after the dissolution of the complexes into the amine. The spectral change was so slow that the time taken for the spectral measurement was negligible. The details of the reaction responsible for this CD spectral change will be reported in the near future.

Results and Discussion

Figures 1-4 show the absorption and CD spectra of the five complexes dissolved in *d*- (or *l*-) α -phenylethylamine or nicotine. In addition, these figures involve the absorption curves in noncoordinating solvents. Numerical data for the absorption