29 Jan 1993

The Electrochemical Characterization of a Platinum Cyclooctadiene Complex as a Guest Molecule in the Presence of ß-Cyclodextrin

Timothy S. Evenson

Recommended Citation

Evenson, Timothy S., "The Electrochemical Characterization of a Platinum Cyclooctadiene Complex as a Guest Molecule in the Presence of ß-Cyclodextrin" (1993). *Opportunities for Undergraduate Research Experience Program (OURE)*. 80.
https://scholarsmine.mst.edu/oure/80

The Electrochemical Characterization of a Platinum Cyclooctadiene Complex as a Guest Molecule in the Presence of β-Cyclodextrin

Submitted to OURE by:
Timothy S. Evenson
Chemistry Department
University of Missouri-Rolla

ABSTRACT

The equilibrium constants for the complexation of the dichloroplatinum-cycloocta-1,5-diene complex with β-cyclodextrin in N,N-dimethylformamide was determined using electrochemical cyclic voltammetry. The constants for both the oxidized and reduced forms of the platinum compound were determined. Model redox experiments were conducted with ferrocene and 1,1'-dimethylferrocene before the platinum compound was studied in order to establish parameters for the experimental method. Also determined was the ratio of the diffusion constants of the guest molecule with and without being complexed with cyclodextrin. In addition to the platinum complex being electrochemically characterized as a guest of cyclodextrin, circular dichroism studies were conducted as well. The results contribute to the understanding of the inclusion-expulsion equilibrium mechanism for the guest-host pair. The results can potentially provide insight for applying inclusion compound chemistry for analytical chemical separations and controlled oxidation-reduction chemistry in specific molecular environments.

INTRODUCTION

Inclusion compounds are currently being widely studied [1]. They result when one molecule, a guest, fits inside another molecule, a host. Inclusion compounds can result from special binding (e.g. hydrogen or ionic bonding) of guest and host, or merely from size and shape (a lock and key mechanism). The inclusion complex will have characteristics different from either the guest or the host alone. These altered chemical properties make inclusion complexes potentially more useful than a free guest molecule. Inclusion complexes are characterized by an equilibrium constant for its formation. The inclusion complex phenomenon could possibly have wide-ranging effects on many different fields [2].

The most widely studied host compounds are cyclodextrins. Cyclodextrins are torus-shaped molecules containg six to nine glucose molecules linked in a ring by 1,4-glycosidic bonds. β-cyclodextrin (CD) contains seven glucose units, and is the focus of this study. It is believed that the only requirement for guests of cyclodextrin is size, although the hydrophobic interior of CD can affect the strength of the binding [3].

It is known that ferrocene compounds form inclusion complexes with CD [4]. It is also known that transition metal complexes of cycloocta-1,5-diene also form inclusion complexes with CD [5]. The transition metal complex should not be confused with the inclusion complex, which is the complex containing both the transition metal complex and cyclodextrin. In this case, the platinum complex is simply the guest portion of the inclusion complex.

The electrochemical properties are among those properties altered by the formation of an inclusion complex, if the guest molecule is electrochemically active (i.e. it can be oxidized or reduced). Cyclic voltammetry measures the current passing through a solution as the voltage applied cycles from one voltage to another and back. The potential is measured versus a standard reference electrode, such as the standard calomel electrode. The data can be plotted on a graph of current vs. potential. This graph is called a cyclic voltammogram. The graph will peak at the formal redox potential of the electroactive chemical. In other words, the current flowing through the system will be greatest when the chemical(s) in solution are being oxidized or reduced.

Two changes occur when cyclodextrin inclusion complexes are formed. First, the peak current is reduced. Second, the potential where this occurs (the half-wave potential) is shifted. Model cyclic voltammograms are shown in Figure 1. The changes in peak current and half-wave potential with the addition of cyclodextrin are used to calculate the equilibrium constant for the formation of the inclusion complex [3]. A model graph of half-wave potential vs. log[CD] is shown in Figure 2.

The formation of the inclusion complex and the electron transfer reaction form a square mechanism. Two sides correspond to the loss and gain of an electron, while the other two sides correspond to the inclusion and expulsion reactions. This square mechanism is shown in Figure 3.

EXPERIMENTAL

N,N-Dimethylformamide, 99% anhydrous, from Aldrich, was used in this experiment due to the solubility, although slight, of cyclodextrin, ferrocenes, and the platinum compound. The ferrocene and 1,1'-dimethylferrocene were also obtained from Aldrich. The dichloroplatinum cycloocta-1,5-diene was obtained from the Johnson Matthey Chemical Company. The electrolyte used was tetrabutyl ammonium perchlorate from Southwestern Analytical. All chemicals were used as received.

The cyclic voltammetry was conducted using an EG&G PARC model 273 potentiostat/galvanostat. The working electrode was solid platinum, and the reference electrode was a standard calomel electrode. The cell used held 25 ml solution, and all solutions were flushed with argon to deoxygenate them.

Cyclic voltammograms (CV's) were run with 1mM ferrocene in 25 ml DMF with CD in concentrations of 0,1,2,. . . . 18,19,20 mM. The electrolyte, tetrabutyl ammonium perchlorate, was present in 0.1M concentration. The solution was subjected to a voltage ranging from +1.0V to -1.0V and back to +1.0V, with the voltage changing at a rate of 20mV/s. The peak currents(i_p) and the half-wave potentials($E_{1/2}$) were recorded for each concentration of cyclodextrin. The graphs of i_p vs. log[CD] and $E_{1/2}$ vs. log[CD] were constructed.

CV's were run for ferrocene under similar conditions. CV's for dichloroplatinum cycloocta-1,5-diene were run from 0.0V to -1.6V and back to 0.0V at the same rate of change of voltage.

To see if free ferrocene and the Fc-CD inclusion complex are reduced and oxidized at different potentials (resulting in two current peaks), 1mM ferrocene was combined with .25mM CD in 25 ml DMF and a CV was run. This was repeated with .50mM CD and .75mM CD.

To help characterize the platinum compound-cyclodextrin inclusion complex, circular dichroism plots were constructed. Pure DMF was the background solvent used. Solutions were made of 2mM platinum compound, 10 mM cyclodextrin, and 2mM platinum compound with 10mM cyclodextrin --all in DMF. The plots involving the platinum compound, the cyclodextrin, and the inclusion complex are given below.

RESULTS

Table 1 gives the values for D_c/D_f , K_2/K_1 , K_1 , and K_2 for the metal complexes with cyclodextrin in dimethyl formamide as calculated with the data from this experiment. The ratio D_c/D_f is equal to the diffusion constant for the inclusion complex divided by the diffusion constant for the free guest molecule. The constant K_1 is the equilibrium constant for the formation of the inclusion complex with the oxidized form of the guest. The constant K_2 is the equilibrium constant for the formation of the inclusion complex using the reduced form of the guest.

TABLE I.

metal complex	D_c/D_f	K_2/K_1	K_1	K_2
ferrocene	.17	.020	43	.86
	.17	.017	71	1.2
1,1'-dimethyl-ferrocene	.12	3e-3	69	.20
	.11	9e-4	73	.06
	.12	1.5e-3	70	.11
$PtCl_2(C_8H_{12})$	.82	211	24	5100
	.82	156	16	2500

The value of K_1 for ferrocene has been reported in the literature as 65 M^{-1} [6].

Table 2 gives the data for a trial of this experiment using 1,1'-dimethylferrocene. Following Table 2 are sample calculations which yield values for the constants of interest.

TABLE 2.

[CD] in mM	i_p (mA)	$E_{1/2}$ (V)
0	.1011	-.1760
1	.0884	-.2340
2	.0860	-.2460
3	.0832	-.2560
4	.0824	-.2680
5	.0775	-.2633
6	.0759	-.2720
7	.0733	-.2780
8	.0689	-.2791
9	.0662	-.2957
10	.0627	-.2900
11	.0604	-.3060
12	.0583	-.3170
13	.0554	-.3280
14	.0518	-.3260
15	.0501	-.3440
16	.0469	-.3274
17	.0437	-.3220
18	.0433	-.3443
19	.0408	-.3369
20	.0394	-.3460
21	.0379	-.3453
22	.0363	-.3420
23	.0345	-.3410
24	.0345	-.3410

$D_c/D_f \dashrightarrow (i_{p\ w/CD} / i_{p\ w/o\ CD})^2 = (.0345/.1011)^2 = .116$

$\ln(K_2/K_1) \dashrightarrow [(E_{1/2\ w/CD} - E_{1/2\ w/o\ CD})^*F] / RT$

$= [(-.341+.176)^*96500] / (8.314\ \text{J/mol-K})(295\text{K})$

$= -6.492$

$K_2/K_1 = 1.52e\text{-}3$

from the straight line portion of the graph $E_{1/2}$ vs. log[CD]:

$y=.590-.144x$

$-.1760 = .590 - .144\ \{[\ln K_1-(1/2)\ln(D_c/D_f)]\}$

$5.319 = \ln K_1+1.077$

$K_1=70$

$K_2 = K_1{}^*(K_2/K_1) = 70^*(1.5e\text{-}3) = .11$

Graph 1 shows the complete set of data points for half-wave potential for ferrocene, and graph 2 shows middle points and a least-squares fit line used in calculations. Graphs 3 and 4 are similar graphs for 1,1'-dimethylferrocene. Graphs 5 and 6 show these plots for dichloroplatinum cycloocta-1,5-diene. Graphs 7 and 8 show the peak current graphs for ferrocene and 1,1'-dimethylferrocene, respectively. These are similar to those predicted in other sources [3,7]. As mentioned previously, the circular dichroism plots are shown after graphs 1-8.

DISCUSSION

The values for the ratio of the inclusion complex diffusion constant to the free guest diffusion constant were determined using the difference in peak current that exists between pure guest (no CD) and the guest with a large excess of CD (20 times the amount of guest). The values for K_2/K_1 were determined using the difference in half-wave potential from the addition of no CD to the addition of a 20-fold excess of CD. The differences in peak current and half-wave potential should be equal to the difference between the highest and lowest values. The constant K_1 was found using the equation of the linear portion of the graph $E_{1/2}$ vs. log[CD]. The ratio K_2/K_1 was then used to solve for K_2. Equations for these calculations came from reference [3]. Unfortunately, multiplying two experimental values to find a third (K_2) may also multiply any error or deviation that exists; this helps to explain the difference in values of K_2.

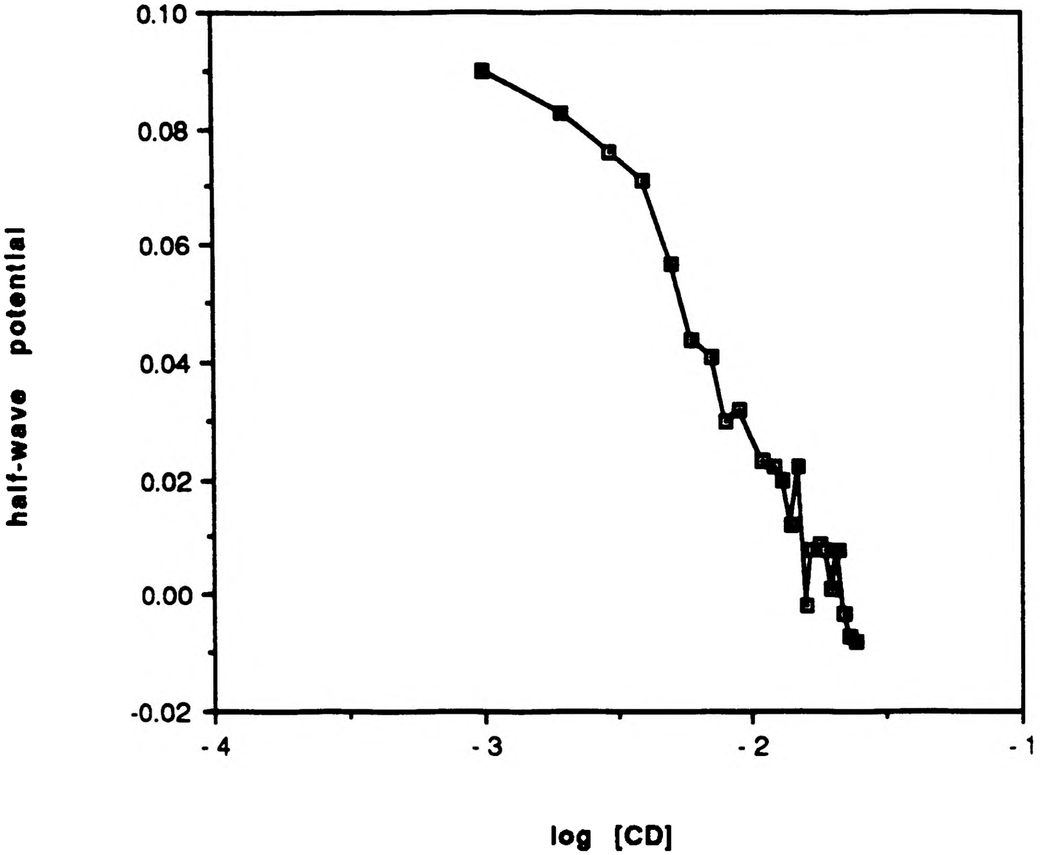
The decrease in peak current resulting from addition of CD to a system is explained by the lower diffusion constant. The lower diffusion constant is explained by the increased bulkiness of the inclusion complex. A shift in the half-wave potential towards more positive values indicates $K_2 > K_1$, while a shift towards the more negative voltages indicates $K_1 > K_2$.

In the cases examined in this experiment, a single electron was transferred to the metal complex--a reduction. In the ferrocene experiments, $Fc^+ \dashrightarrow Fc$. In the platinum complexes, a neutral complex took on a negative charge. The results of this experiment show that the charged species are bound by cyclodextrin more tightly than their uncharged counterparts. This increased affinity for cyclodextrin implies that the charged species are stabilized by the cyclodextrin host molecules.

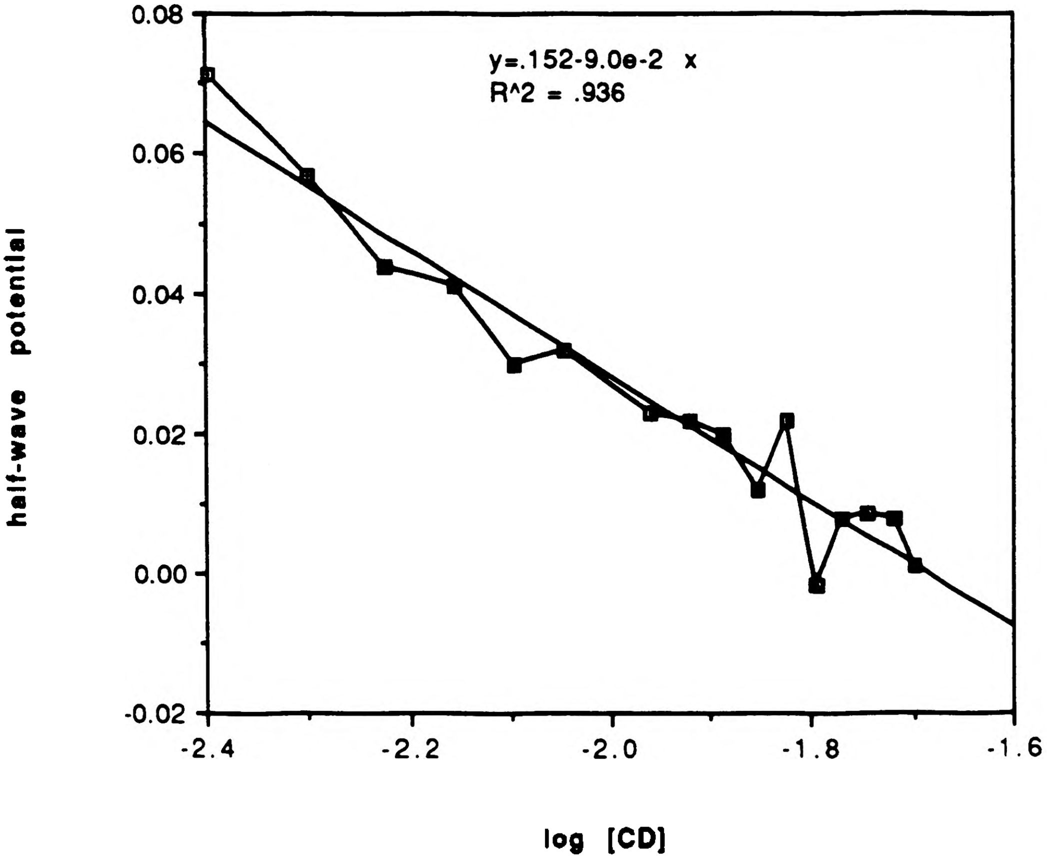
The fact that only one peak is seen when complexed and free ferrocene are reduced yields one of two conclusions: either 1. ferrocene is reduced just after dissociation from CD, or 2. the inclusion complex is reduced at the same potential as the guest. The first conclusion has been made previously in other reports [6].

The circular dichroism plots prove that combining the platinum compound with cyclodextrin in DMF produces an inclusion complex. The plot of the platinum compound mixed with cyclodextrin is different than the sum of the two other plots (Pt compound alone and CD alone). If the mixture of the guest and host did not form an inclusion complex, and was simply a mixture of the chemicals in solution, then the circular dichroism plot for the mixture would be the sum of the plots for each individual solute. The fact that this is not the case proves that the mixture of these two chemicals is, in fact, a new chemical--an inclusion complex.

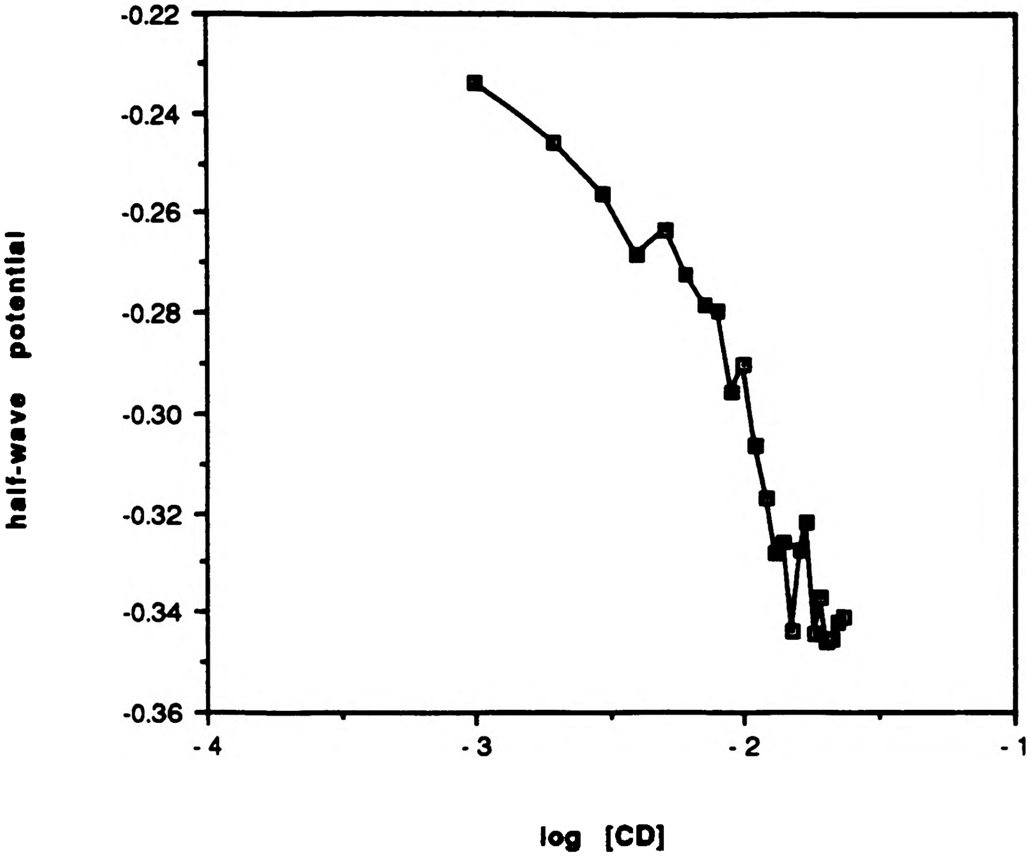
graph 1
ferrocene



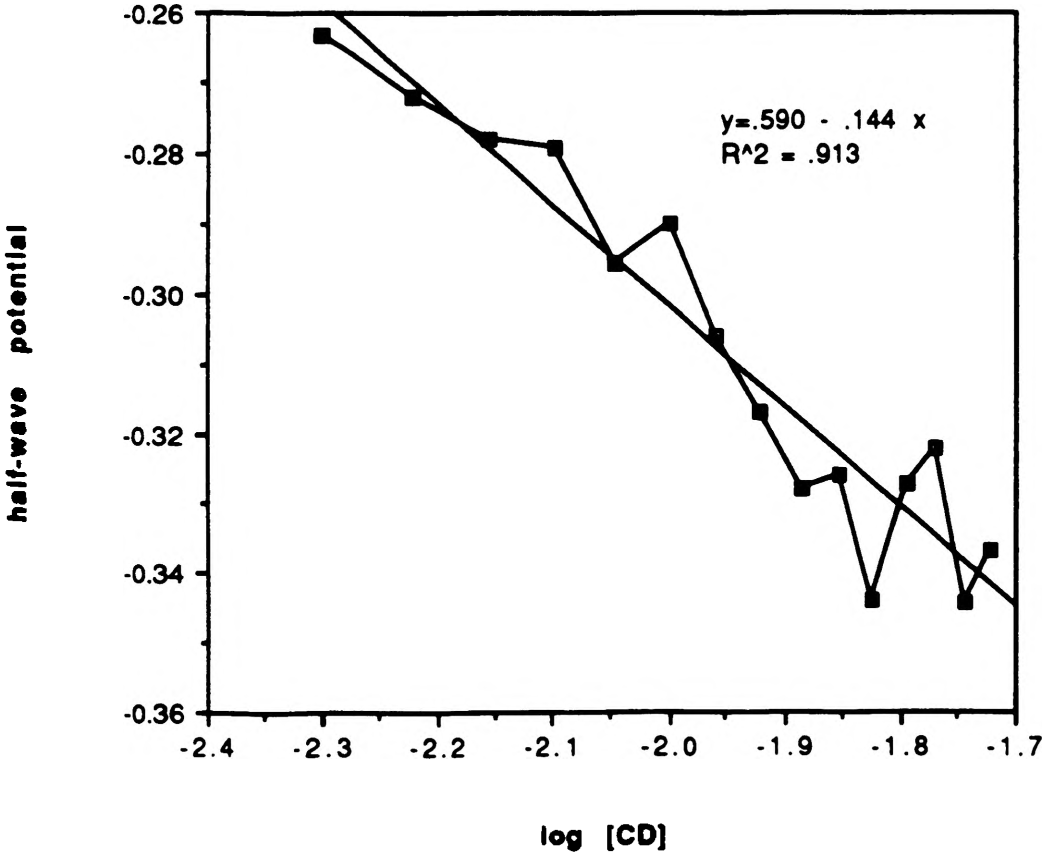
graph 2
ferrocene



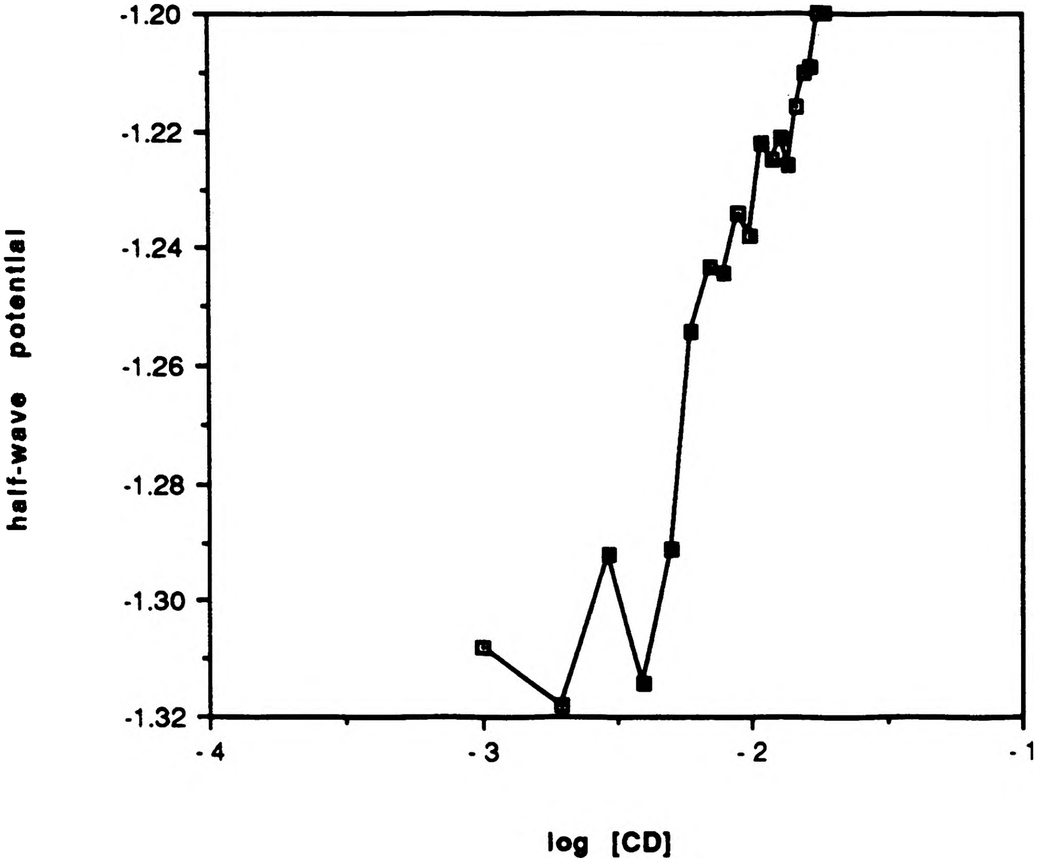
graph 3
1,1-dimethylferrocene



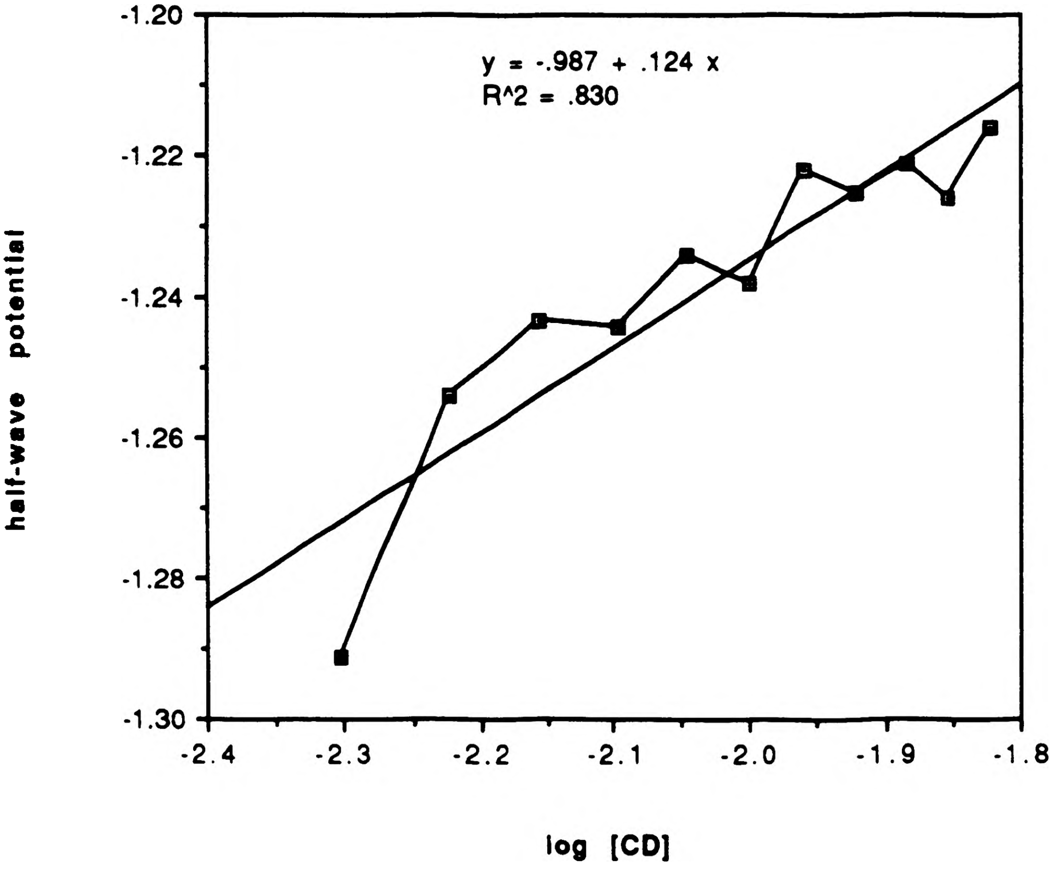
graph 4
1,1'-dimethylferrocene

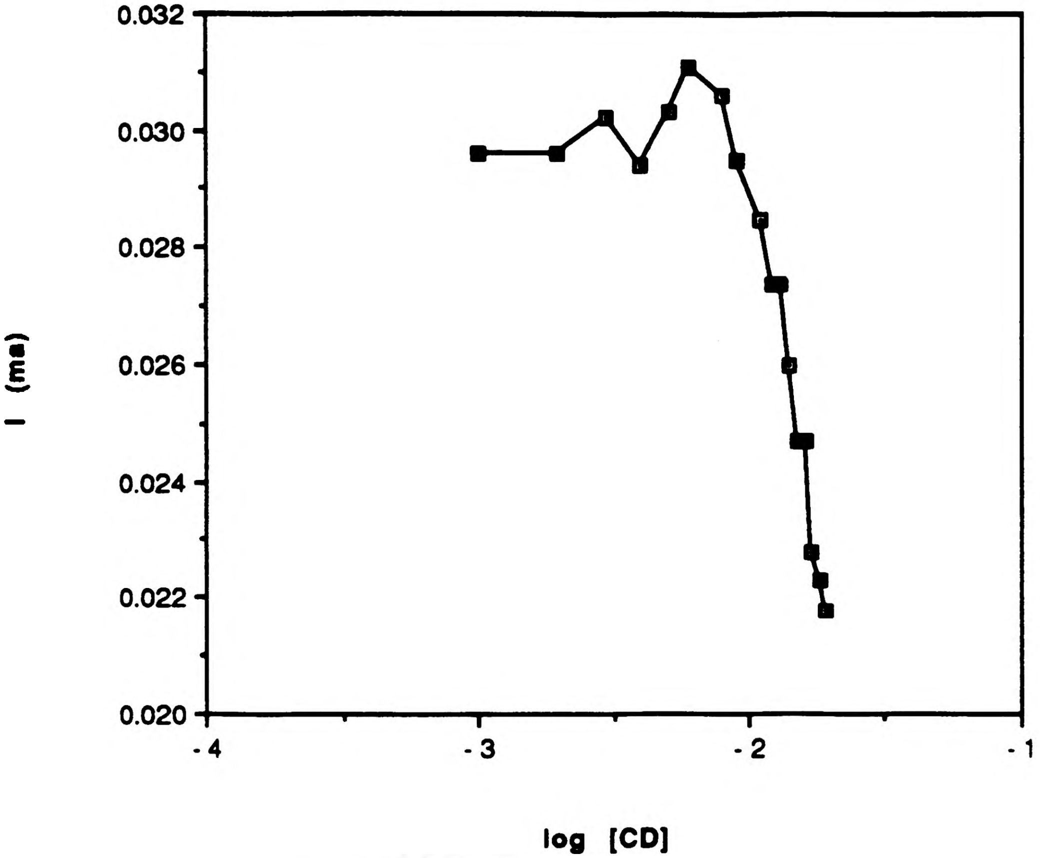


graph 5
dichloroplatinum cycloocta-1,5-diene

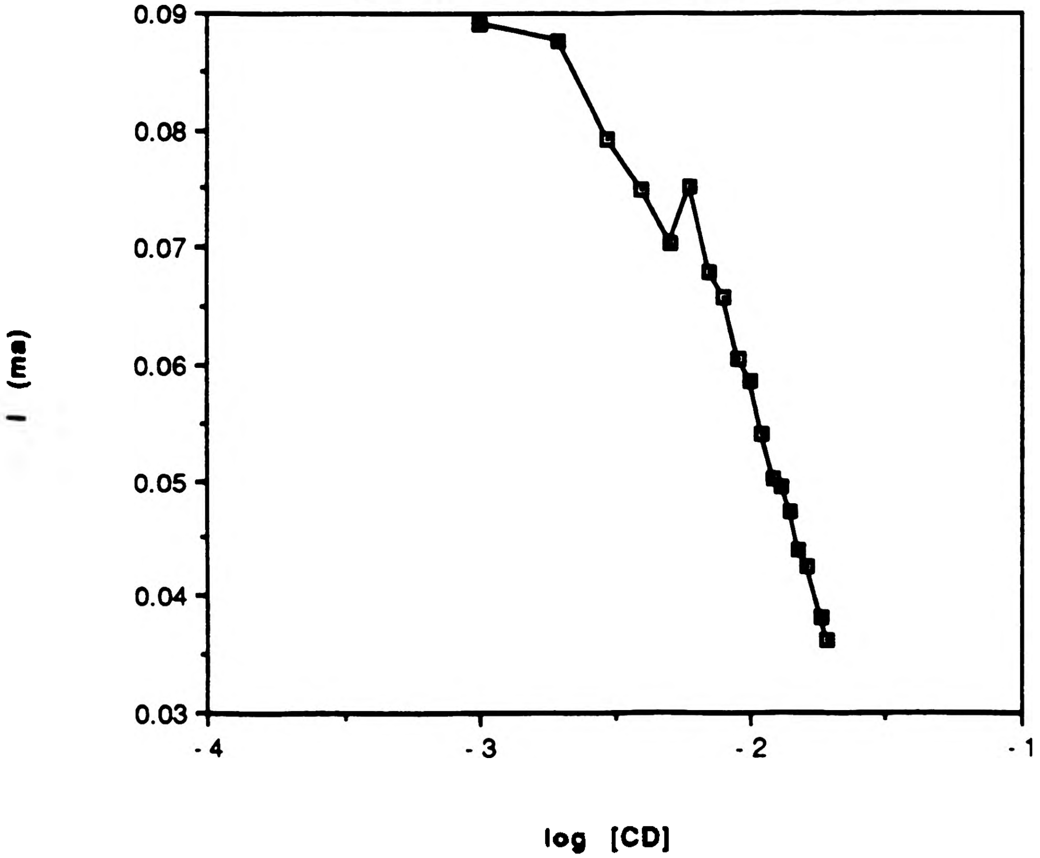


graph 6
dichloroplatinum cycloocta-1,5-diene

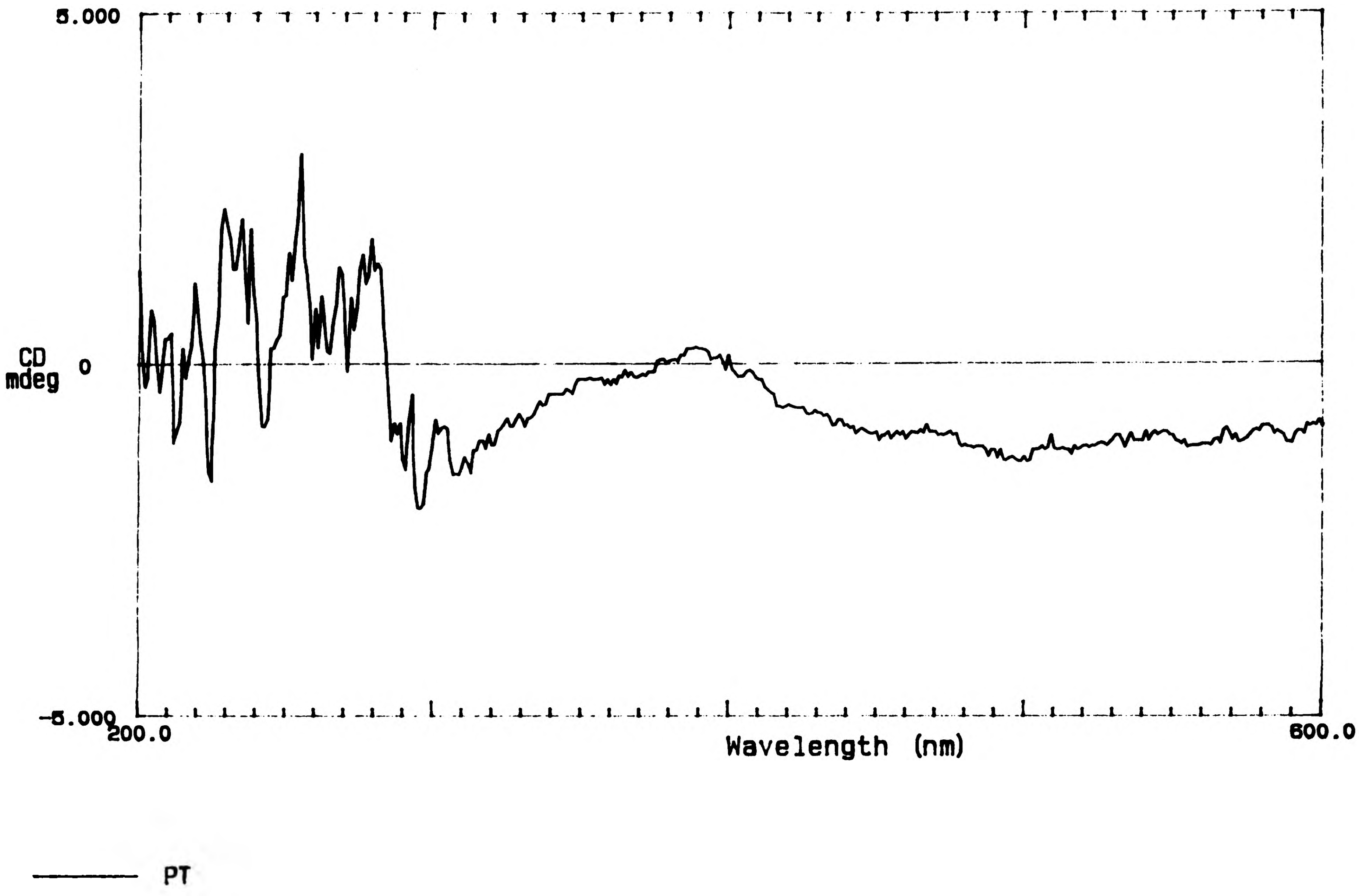


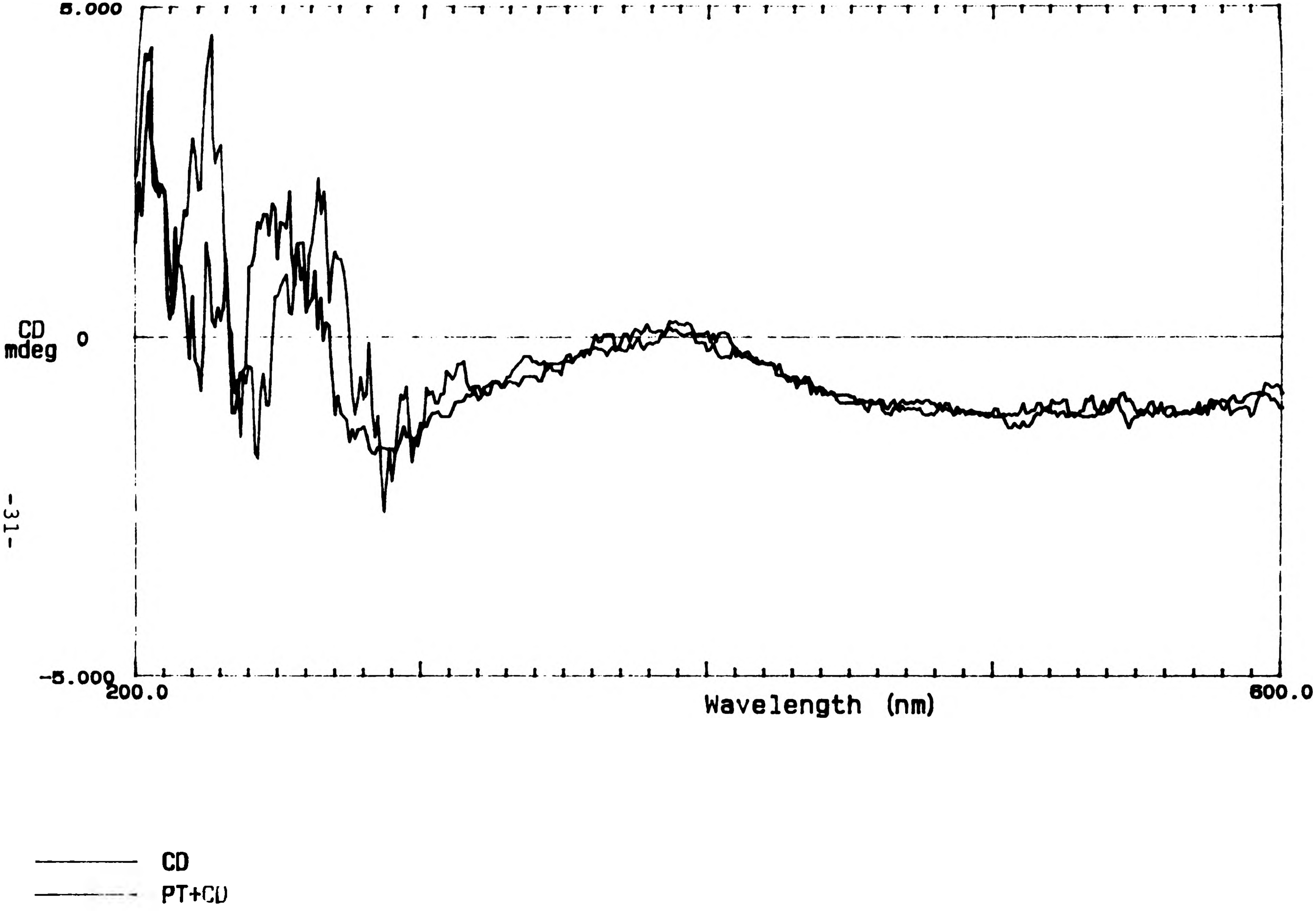


grapn 7
ferrocene
peak current vs. log [CD]



graph 8
1,1'-dimethylferrocene
peak current vs log [CD]


5.000
CD
mdeg
0
-5.000
200.0
600.0
Wavelength (nm)
PT


5.000
CD
mdeg
0
-5.000
200.0
600.0
Wavelength (nm)
CD
PT+CD

REFERENCES

1. *Inclusion Chemistry*, volume 1, ed. Atwood, et.al., Academic Press, Orlando, Florida, 1984, pp 12-28.

2. *Inclusion Chemistry*, volume 3, ed. Atwood, et.al., Academic Press, Orlando, Florida, 1984, pp 331-391.

3. T.Matsue, et.al., Journal of Inclusion Phenomena, 2, 1984, p547.

4. A.Ryabov, et.al., Bioelectrochemistry and Bioenergetics, 24, 1990, p257.

5. A.Harada and S.Takahashi, Journal of Macromolecule Science, A26, 1989, p373.

6. V.Strelets, et.al., Journal of Electroanalytical Chemistry, 310, 1991, p179.

7. T.Matsue, et.al., Journal of the American Chemical Society, 107, 1985, p3411.

ACKNOWLEDGMENTS

I would like to thank Dr. H.L. Collier for his advice and support. I would also like to thank the Opportunities for Undergraduate Research Experience (OURE) organization for their funding of this research.