

## On the Outer-sphere Complexity of the (-)-Trisethylene-diamineplatinum(IV) Ion in Acid and Basic Aqueous Solutions

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Light absorption and circular dichroism spectra have been determined for the ions (-)-Pt en<sub>3</sub><sup>4+</sup> and (-)-Pt en<sub>2</sub>(en-H)<sup>3+</sup>. From the changes of these spectra, when the concentrations of different electrolytes were varied in the solutions, it can be shown that outer-sphere complexes are formed.

For the Pt en<sub>3</sub><sup>4+</sup>-SO<sub>4</sub><sup>2-</sup> system three such complexes probably exist, for the Pt en<sub>3</sub><sup>4+</sup>-Cl<sup>-</sup> system at least one complex has been found, and for the Pt en<sub>2</sub>(en-H)<sup>3+</sup>-S<sub>2</sub>O<sub>3</sub><sup>2-</sup> at least two outer-sphere complexes have been discovered. The nature of the changes of the spectra following outer-sphere coordination is discussed.

In recent years much work has been devoted to investigations of the degree of the outer-sphere complexity of inert hexamine complexes. Mostly, the ions Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and Co en<sub>3</sub><sup>3+</sup> have been studied. With various methods different results have been reached; *e.g.*, a spectrophotometric investigation<sup>1</sup> seems to indicate that only one chloride ion associates with the Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> ion up to rather high concentrations of ligand, whereas anionic exchanger distribution experiments<sup>2</sup> have been used to argue that four chloride ions can associate with the said cobalt ion.

In view of these and similar differing results it has been considered interesting to investigate the outer-sphere complexity of inert platinum(IV) ammine complexes. As the measuring of the circular dichroism of optically active central groups seems to be an extremely sensitive tool for the investigation of outer-sphere complexity,<sup>3</sup> the (-)-Pt en<sub>3</sub><sup>4+</sup> ion was chosen for this work.

Previously, Nyman and Plane<sup>4</sup> and Giedt and Nyman<sup>5</sup> have investigated the outer-sphere complexity of the Pt en<sub>3</sub><sup>4+</sup> ion by a spectrophotometric technique. These authors find reason to believe that only one association step occurs for a series of both one- and two-valent ions. This result seems rather unlikely for such a highly charged central group. It must be remem-

bered, however, that the method used by these authors is known to give very uncertain results. It is, as a rule, not possible to exclude the existence of more than one complex from the form of the curve describing the variation of optical density as the ligand concentration increases. This fact has been pointed out by many authors,<sup>6-9</sup> and is related to the monotonous increase of extinction coefficients of the successive complexes that may be formed. The circular dichroism coefficients, on the other hand, can be both greater and smaller than the ones for the free central group, depending on the number of outer-sphere ligands attached.<sup>10</sup> This makes it reasonable to believe that measurements of circular dichroism will give more easily interpreted results also in the present case.

#### EXPERIMENTAL DETAILS AND CONDITIONS OF MEASUREMENT

The circular dichroism was measured with a Roussel-Jouan Dichrograph, model A, with a thermostated cell compartment. This was kept at 20°C. All solutions were allowed to attain temperature equilibrium in a 20.0° water thermostat before measurement. The absorption measurements were performed with a Unicam S. P. 700, also at 20°C. These instruments were used for the experiments carried out at the University of East Anglia.

The experiments carried out at the University of Lund were performed with a Model B Dichrograph of the same company and a Beckman DK-1 recording spectrophotometer, both instruments being thermostated as above.

*Chemicals used.* (-)-Pt en<sub>3</sub>Cl<sub>4</sub>·3H<sub>2</sub>O was prepared from reagent quality chemicals (B.D.H.) following the procedures given by Werner.<sup>11</sup> It was twice reprecipitated with ammonium(+)-tartrate and recrystallized. The specific rotations,  $[\alpha]_D = -89^\circ$  and  $[\alpha]_F = -139^\circ$ , correspond satisfactorily with the values given by Werner,  $-88^\circ$  and  $-133^\circ$ , respectively. The complex was then transferred to the perchlorate form by treating an aqueous solution, containing some perchloric acid, with the stoichiometric amount of silver perchlorate. The precipitate was filtered off and the solution diluted to a known volume. A stock solution then resulted, with the composition  $C(-)\text{-Pt en}_3(\text{ClO}_4)_4 = 63$  mM,  $C_{\text{HClO}_4} = 50$  mM.

All other chemicals were of the purest type available (B.D.H.). The sodium perchlorate was of the "chloride free" type. It was recrystallized, following the prescriptions given by Fronæus.<sup>12</sup>

*The acid-base equilibrium.* The acidic properties of the Pt en<sub>3</sub><sup>4+</sup> ion have been investigated by Grinberg and coworkers<sup>13</sup> with a potentiometric technique. These measurements give  $\text{p}K_1 = 5.5$ ,  $\text{p}K_2 = 9.7$ , and  $\text{p}K_3 \approx 10.7$  (quoted from the work of Jørgensen<sup>14</sup>).

As we want to compare the possible outer-sphere complexity of the Pt en<sub>3</sub><sup>4+</sup> and the Pt en<sub>2</sub>(en-H)<sup>3+</sup> ions, our purpose is to find a buffer system for which only the Pt en<sub>2</sub>(en-H)<sup>3+</sup> ion is present in large amounts, the Pt en<sub>3</sub><sup>4+</sup> and Pt en(en-H)<sub>2</sub><sup>2+</sup> species

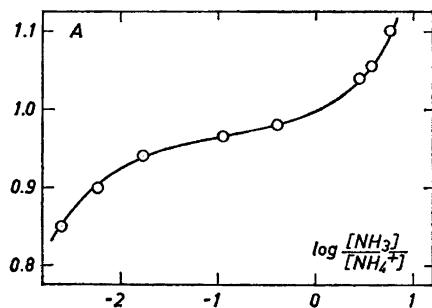


Fig. 1. Variation of optical density of a 0.63 mM Pt en<sub>3</sub>(ClO<sub>4</sub>)<sub>4</sub> solution and cell thickness 1 cm with  $[\text{NH}_3]/[\text{NH}_4^+]$ .

being present in only negligible amounts. Furthermore, there is an obvious requirement that this buffer system shall not contain species which are liable to form outer-sphere complexes with any of the investigated platinum ions.

The  $pK$ -values, quoted above, suggest that the ammonium-ammonia buffer system should be a good one. Also in another respect it seems to be acceptable, as earlier works<sup>15</sup> have indicated that the  $\text{Co}(\text{NH}_3)_6^{3+} - \text{NH}_3$  complexity is a very weak one. However, the greater acidity of the platinum complexes should make these more apt to form hydrogen bonds with a suitable acceptor than the  $\text{Co}(\text{NH}_3)_6^{3+}$  ion is. Hence there may be a greater degree of outer-sphere ammonia complexity for the present systems than for that investigated earlier. Nevertheless, the ammonia buffer system seems to be the best choice available. In order to determine a ratio of  $[\text{NH}_4^+]:[\text{NH}_3]$  that would ensure the abovementioned conditions, the change of optical density of a solution containing 0.63 mM  $\text{Pt en}_3(\text{ClO}_4)_4$ , 0.45 M  $\text{NH}_4\text{ClO}_4$ , 1.5 M  $\text{NaClO}_4$  and  $C$  M  $\text{NH}_3$  was measured. In Fig. 1 the optical densities at 32.9 kK corresponding to the maximum of absorption of the  $\text{Pt en}_2(\text{en-H}^{2+})$  ion, are plotted against  $\log [\text{NH}_3]/[\text{NH}_4^+]$ .

It may be seen that there exists a region,  $-0.4 > \log [\text{NH}_3]/[\text{NH}_4^+] > -1.4$ , where the optical density is approximately constant. This means that we have almost only the  $\text{Pt en}_2(\text{en-H}^{2+})$  ion in this buffer range. For greater concentrations of ammonia the position of maximum absorption was slightly shifted towards higher frequencies. This indicates — as does the increase of the optical density at 32.90 kK — that the next protolysis step begins to be appreciable when  $\log [\text{NH}_3]/[\text{NH}_4^+] > 0$ . However, as one can estimate from the bending of the curve (Fig. 1) that only a small fraction of the species  $\text{Pt en}(\text{en-H})_2^{2+}$  is at hand for  $\log [\text{NH}_3]/[\text{NH}_4^+] = 0$ , this composition of the buffer was selected for the following investigations of the outer-sphere complexity. It can probably be taken for granted that because of the smaller charge of the  $\text{Pt en}(\text{en-H})_2^{2+}$  ion the degree of outer-sphere complexity of this ion will be smaller than that of the main platinum species of such solutions,  $\text{Pt en}_2(\text{en-H}^{2+})$ . Hence any observations made will be ascribed to complex formation between this latter ion and the ligands in question.

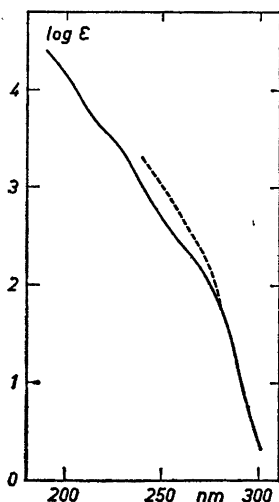


Fig. 2. Absorption spectrum of the (—)  $\text{Pt en}_3^{4+}$  ion in water (---) and in 0.9 M  $\text{Na}_2\text{SO}_4$  solution.

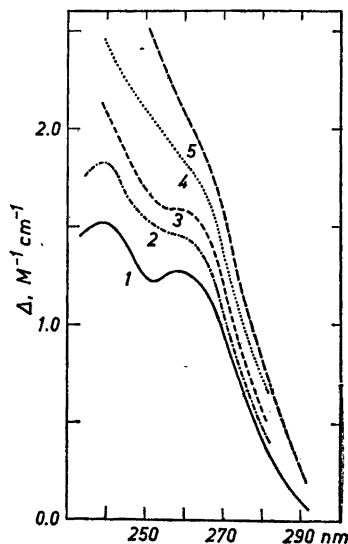


Fig. 3. Circular dichroism curves for the free (—)  $\text{Pt en}_3^{4+}$  ion (1) and for solutions with  $C_{\text{NaCl}} = 0.18$  M (2), 0.39 M (3), 1.41 M (4), and 2.65 M (5).

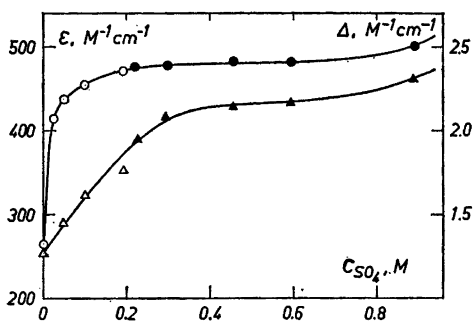


Fig. 4. The functions  $\epsilon$  and  $\Delta$  of the  $(-)\text{-Pt en}_3^{4+}$  ion as a function of the sulphate concentration. ( $\lambda = 260$  nm).

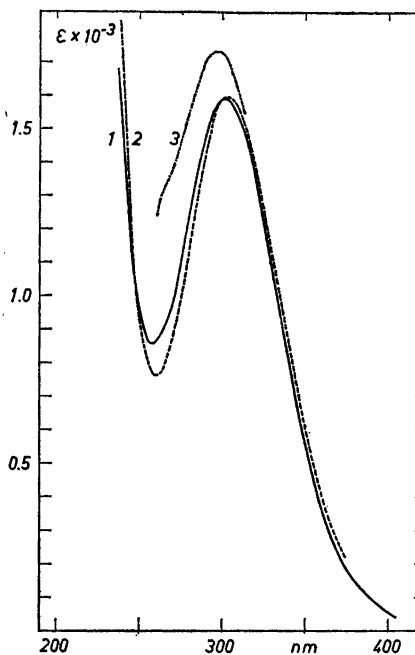


Fig. 5. Absorption spectra of the  $(-)\text{-Pt en}_2(\text{en-H})^{3+}$  ion in the ammonium-ammonia buffer (1), in buffer solutions with  $C_{\text{NaCl}} = 1$  M (2) and  $C_{\text{Na}_2\text{S}_2\text{O}_8} = 0.28$  M (3).

Also, considering the possibility that the outer-sphere complexing probably favours the fourvalent  $\text{Pt en}_3^{4+}$  ion compared to the base form  $\text{Pt en}_2(\text{en-H})^{3+}$  it was considered cautious to operate in a somewhat higher pH-range than is really the optimum one from the presented measurements.

#### A QUALITATIVE COMPARISON BETWEEN THE ACID AND THE BASE FORMS OF $\text{Pt en}_3^{4+}$

In an acid medium the circular dichroism and the absorption spectra were measured for the chloride and the sulphate systems. (No sodium perchlorate was added to keep the ionic strength constant.) Appreciable changes were found for the absorption spectrum in agreement with the results of Nyman and coworkers<sup>4-5</sup> as well as for the circular dichroism spectrum (Figs. 2 and 3). Fig. 4 shows how the absorption and CD data for the sulphate system depend on the concentration of the sulphate ions. In the sulphate case the measurements have been carried up to a much higher concentration than was the case in the earlier investigations.<sup>4,5</sup> In the case of absorption one can see a concentration region of almost constant absorption, followed by an increase. The relation between the concentration dependence of the circular dichroism

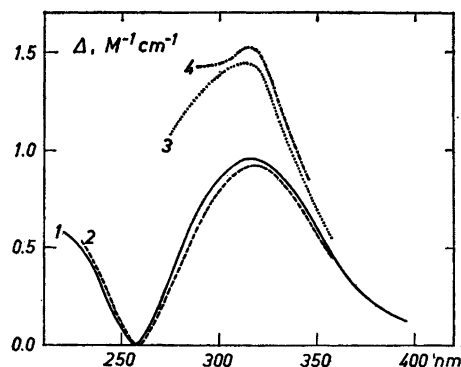


Fig. 6. Circular dichroism curves of the  $(-)\text{-Pt en}_3(\text{en-H}^{3+})$  ion in the ammonium-ammonia buffer (1), in buffer solutions with  $C_{\text{NaCl}} = 1 \text{ M}$  (2),  $C_{\text{Na}_2\text{S}_2\text{O}_3} = 0.28 \text{ M}$  (3), and  $C_{\text{Na}_2\text{S}_2\text{O}_3} = 0.83 \text{ M}$  (4).

and that of the absorption will be dealt with in greater detail in the next section of this paper.

In Figs. 5 and 6 are the absorption spectra and the circular dichroism spectra, respectively, given for the base form with various amounts of chloride and thiosulphate ions added to the solution. In contrast to what was the case for the acid form the circular dichroism does not seem to be influenced very much by the addition of chloride ions. One can observe, however, a shift of the absorption maximum towards longer wavelengths, which effect can also be found in the CD spectrum.

The influence of thiosulphate ions, on the other hand, is pronounced. The most obvious change in the absorption spectrum (Fig. 5) is a distinct shift of the absorption maximum towards shorter wavelengths when thiosulphate ions are added. This also holds for the CD-spectrum. There is also a shoulder at 265 nm in the absorption spectrum for solutions of high thiosulphate concentration that is missing for solutions of more moderate thiosulphate concentrations. Because of the high absorption of the thiosulphate ion itself it was not possible to confirm this effect for very high concentrations. The appearance of a second absorption band at a somewhat lower wavelength is also indicated in the CD spectrum (Fig. 6,  $C_{\text{S}_2\text{O}_3^-} = 0.83 \text{ M}$ ).

#### A DETAILED EXAMINATION OF THE SULPHATE AND THE CHLORIDE SYSTEMS OF THE $(-)\text{-Pt en}_3^{4+}$ ION

As may be seen from the recorded spectra, the circular dichroism coefficients of the  $(-)\text{-Pt en}_3^{4+}$  ion in the spectral region available are of the order of  $1 \text{ M}^{-1} \text{ cm}^{-1}$  or less. The bands observed with maximum values at about 260 nm and 240 nm correspond to the ligand field created  $d-d$  transitions, which in the pure octahedral case are  $A_{1g} \rightarrow T_{1g}$  and  $A_{1g} \rightarrow T_{2g}$ , respectively. However, whereas the corresponding absorption bands of, e.g., the Co(III) analogue lie well outside the ligand-metal charge transfer bands, the contrary is the case here. As a matter of fact the absorption bands corresponding to the  $d-d$  transitions are almost hidden by the charge transfer absorption of the  $\text{Pt en}_3^{4+}$  ion (Fig. 2). Hence the cell thickness or the concentration of

the sample had to be greatly reduced, compared to what can be used when measuring cobalt(III) ammines. Consequently, the deflections on the Dichrograph are of the order of 10–20 mm only. This caused considerable uncertainties in the recorded dichroism. It is therefore not possible to make a complete analysis of the complexity of any system even if the relative change of the circular dichroism may be as great as was the case in the  $\text{Co en}_3^{3+} - \text{SeO}_3^{2-}$  system.<sup>16</sup> Thus it is necessary to confine the investigation to an interpretation of the relative change of the circular dichroism, as the concentration of the outer-sphere ligand is increased.

As mentioned in the introduction, there is an intrinsic difficulty in trying to detect the existence of more than one complex from absorption data under the experimental conditions used here, *i.e.*  $C_M \ll C_L$ . In order to try to evade this difficulty, the following comparison between CD and absorption data has been undertaken.

*Notations:*

CD = observed circular dichroism

$A$  = observed optical density

$A_n = (\varepsilon_i - \varepsilon_r)_n$ , *i.e.* circular dichroism coefficient of the complex  $\text{ML}_n$

$\varepsilon_n$  = extinction coefficient of the complex  $\text{ML}_n$

$d$  = cell thickness

$\beta_n$  = stability constant of  $\text{ML}_n$  where  $\beta_0 = 1$

$\Delta = \text{CD}/d \cdot C_M$

$\varepsilon = A/d \cdot C_M$

We then have

$$\text{CD} = d \cdot \sum_{n=0}^N [\text{ML}_n] A_n \quad (1)$$

$$A = d \cdot \sum_{n=0}^N [\text{ML}_n] \varepsilon_n \quad (2)$$

or

$$\Delta = \frac{\sum_{n=0}^N A_n \beta_n [\text{L}]^n}{\sum_{n=0}^N \beta_n [\text{L}]^n} \quad (3)$$

$$\varepsilon = \frac{\sum_{n=0}^N \varepsilon_n \beta_n [\text{L}]^n}{\sum_{n=0}^N \beta_n [\text{L}]^n} \quad (4)$$

Forming the expressions  $\Delta - \Delta_0$  and  $\varepsilon - \varepsilon_0$  and taking the ratio,  $\varrho$ , between them, one obtains

$$\varrho = \frac{\Delta - \Delta_0}{\varepsilon - \varepsilon_0} = \frac{\sum_{n=1}^N (A_n - \Delta_0) \beta_n [\text{L}]^n}{\sum_{n=1}^N (\varepsilon_n - \varepsilon_0) \beta_n [\text{L}]^n} \quad (5)$$

It follows from eqn. (5) that if only one complex exists the ratio  $\rho$  will have a constant value for all concentrations  $[L]$ . This will hold even if there is a drastic variation of the stability constant, caused by the nonconstancy of the ionic strength. Also, even if  $(\epsilon_i - \epsilon_r)_1$  and  $\epsilon_1$  will vary with  $C_L$  because of the variation of the medium's refractive index and the like, it seems reasonable that the ratio between these quantities will be much more insensitive to such factors. Thus, if the ratio  $\rho$  is found to vary with  $[L]$ , *i.e.*  $C_L$ , as  $C_L > C_M$ , one can infer that more than one complex exist.

Table 1. The Pt  $en_3^{4+} - SO_4^{2-}$  system. Determination of the function  $\rho = (\Delta - \Delta_0)/(\epsilon - \epsilon_0)$ . Upper set of data: UEA ( $C_M = 7.5$  mM), lower set: LU ( $C_M = 6$  mM).

$C_{SO_4^{2-}}$ (M)	$\lambda = 250$ nm			$\lambda = 260$ nm			$\lambda = 270$ nm		
	$\Delta M^{-1}cm^{-1}$	$\epsilon M^{-1}cm^{-1}$	$\rho \times 10^3$	$\Delta M^{-1}cm^{-1}$	$\epsilon M^{-1}cm^{-1}$	$\rho \times 10^3$	$\Delta M^{-1}cm^{-1}$	$\epsilon M^{-1}cm^{-1}$	$\rho \times 10^3$
0	1.24	495		1.27	265		0.96	140	
0.05	1.63	870	1.0	1.45	440	1.2	1.04	215	1.1
0.10	1.86	930	1.4	1.62	455	1.8	1.18	220	2.8
0.19	2.06	960	1.8	1.77	475	2.4	1.30	225	4.2
0.22	2.43	960	2.5	1.95	475	3.2	1.38	225	5.1
0.30	2.45	975	2.5	2.08	480	3.8	1.44	225	5.9
0.45	2.73	990	3.0	2.14	480	4.1	1.51	220	6.9
0.59	2.75	1000	3.0	2.17	480	4.2	1.53	220	7.2
0.89	3.01	1030	3.3	2.31	500	4.5	1.54	230	6.6

Table 2. The Pt  $en_3^{4+} - Cl^-$  system. Determination of the function  $\rho = (\Delta - \Delta_0)/(\epsilon - \epsilon_0)$ . Upper set of data: LU ( $C_M = 6$  mM), lower set: UEA ( $C_M = 7.5$  mM).

$C_{Cl^-}$ (M)	$\lambda = 250$ nm			$\lambda = 255$ nm			$\lambda = 260$ nm		
	$\Delta M^{-1}cm^{-1}$	$\epsilon M^{-1}cm^{-1}$	$\rho \times 10^3$	$\Delta M^{-1}cm^{-1}$	$\epsilon M^{-1}cm^{-1}$	$\rho \times 10^3$	$\Delta M^{-1}cm^{-1}$	$\epsilon M^{-1}cm^{-1}$	$\rho \times 10^3$
0	1.24	495		1.25	355		1.27	265	
0.02	1.36	570	1.6	1.34	400	2.0	1.31	285	2
0.22	1.69	805	1.4	1.59	560	1.7	1.56	385	2.4
0.42	1.76	925	1.2	1.66	635	1.5	1.57	445	1.7
0.52	1.85	965	1.3	1.66	665	1.3	1.63	470	1.8
0.62	1.89	1000	1.3	1.76	685	1.6	1.64	485	1.7
0.92	2.06	1085	1.4	1.89	745	1.7	1.75	530	1.8
1.22	2.18	1155	1.4	2.03	795	1.8	1.85	570	1.9
1.52	2.24	1220	1.4	2.08	850	1.7	1.96	600	2.1
1.82	2.36	1275	1.4	2.19	905	1.7	1.91	625	1.8
0.18	1.55	770	1.1				1.45	365	1.8
0.39	1.74	905	1.2				1.58	435	1.8
0.60	1.86	995	1.2				1.63	480	1.7
0.88	1.90	1075	1.1				1.73	525	1.8
1.41	2.11	1200	1.2				1.83	590	1.7
1.95	2.29	1300	1.3				1.98	640	1.9

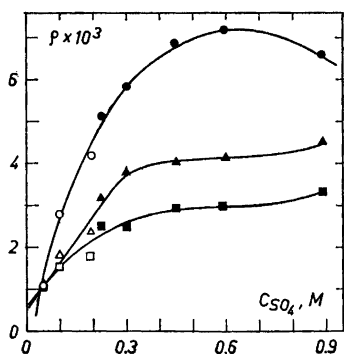


Fig. 7. The function  $\rho$  (eqn. 5) for the (—)-Pt  $\text{en}_3^{4+}$ — $\text{SO}_4^{2-}$  system.  $\circ$ :  $\lambda = 270$  nm,  $\triangle$ :  $\lambda = 260$  nm,  $\square$ :  $\lambda = 250$  nm. Filled points refer to LU work ( $C_{\text{Pt}} = 6$  mM), open points to UEA work ( $C_{\text{Pt}} = 7.5$  mM).

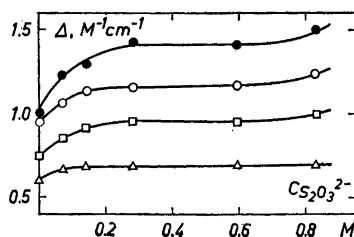


Fig. 8. The function  $\Delta$  for the (—)-Pt  $\text{en}_3(\text{en-H})^{3+}$ — $\text{S}_2\text{O}_3^{2-}$  system.  $\bullet$ : 320 nm,  $\circ$ : 330 nm,  $\square$ : 340 nm, and  $\triangle$ : 350 nm.  $C_{\text{Pt}} = 10$  mM.

This approach has been applied to the chloride and the sulphate systems of the Pt  $\text{en}_3^{4+}$  in slightly acid medium. As the criterion stated above is independent of changes of the stability constants, the experiments were performed without trying to keep the ionic strength constant. In this way the results can be directly compared with those of Nyman and coworkers. The results are collected in Tables 1 and 2. In Fig. 7 the function  $\rho$  is represented for various values of  $C_{\text{SO}_4}$ . It is clearly seen that this function is not constant and thus we can conclude from the arguments above that more than one complex exist in solution. Indeed, if two complexes were present one should expect that for large values of  $C_{\text{SO}_4}$  the function  $\rho$  should approach the constant value  $(\Delta_2 - \Delta_0)/(\epsilon_2 - \epsilon_0)$ . This is not the case. One sees a gradual decrease of the slope of the function  $\rho$ , and a tendency towards levelling off to a zero value in the sulphate concentration range 0.4–0.6 M. Thereafter, either an increase ( $\lambda = 250, 260$  nm) or a decrease ( $\lambda = 270$  nm) of the slope takes place. One easily deduces, however, that for a system of only two complexes the function  $\rho$  will have no extremum or inflection for any finite value of  $[\text{L}]$ .

Let us suggest, therefore, that this implies that a third outer-sphere complex is being formed, where  $\Delta_3 > \Delta_2$  for  $\lambda = 250, 260$  nm and  $\Delta_3 < \Delta_2$  for  $\lambda = 270$  nm.

We can then conclude that the first and the second complexes exist in appreciable amounts in the range  $0 < C_{\text{L}} < 0.4$  M and that the second and the third complexes exist together for  $C_{\text{L}} > 0.6$  M.

The results for the chloride system, on the other hand, are more difficult to interpret. Within the experimental errors, the function  $\rho$  has a constant value (Table 2). For such a case there are two possibilities, namely: *pro primo* that only one complex exists for all values of  $[\text{L}]$ , and *pro secundo* that more



Table 3. The Pt en<sub>2</sub>(en-H)<sup>3+</sup>–S<sub>2</sub>O<sub>3</sub><sup>2-</sup> system. Determination of the function  $\rho = (\Delta - \Delta_0)/(\varepsilon - \varepsilon_0)$ . All data UEA. Subscripts of  $\Delta$  and  $\varepsilon$  indicate wavelength of measurement.

$C_{S_2O_3^{2-}}$ (M)	$\Delta_{280}$ M <sup>-1</sup> cm <sup>-1</sup>	$\varepsilon_{286}$ M <sup>-1</sup> cm <sup>-1</sup>	$\rho \times 10^3$	$\Delta_{290}$ M <sup>-1</sup> cm <sup>-1</sup>	$\varepsilon_{294}$ M <sup>-1</sup> cm <sup>-1</sup>	$\rho \times 10^3$	$\Delta_{330}$ M <sup>-1</sup> cm <sup>-1</sup>	$\varepsilon_{270}$ M <sup>-1</sup> cm <sup>-1</sup>	$\rho \times 10^3$
0	0.51	1330		0.68	1530		0.86	980	
0.07							1.07	1140	1.3
0.14	1.00	1570	2.1	1.13	1685	2.9	1.11	1265	0.9
0.29	1.16	1640	2.1	1.29	1730	3.1	1.16	1385	0.7
0.83				1.43	1770	3.1			

than one complex exist within the given concentration range, but that it so happens that

$$\frac{\Delta_n - \Delta_0}{\Delta_1 - \Delta_0} = \frac{\varepsilon_n - \varepsilon_0}{\varepsilon_1 - \varepsilon_0} \quad (6)$$

so that all terms containing powers of [L] will divide away. It is therefore not possible to make any definite statements in this case.

There are, however, some indications that the second alternative is the true one. For the wavelengths 260 and 255 nm, the difference  $\rho - \rho_{\text{mean}}$  is mainly positive in the range  $0 < C_L < 0.4$  M and mainly negative in the range  $0.4 < C_L < 0.7$  M and positive or close to zero for  $C_L > 0.7$  M. This could mean that there is a small variation of  $(\Delta_n - \Delta_0)/(\Delta_1 - \Delta_0)$  compared to  $(\varepsilon_n - \varepsilon_0)/(\varepsilon_1 - \varepsilon_0)$ , but that this variation is too small to be detected for the other wavelengths. In such a case the second complex should be the dominating species in the concentration range  $0.4 < C_L < 0.7$  and a third complex should be present also for  $C_L > 0.7$  M.

Also, in the case of the thiosulphate system of the protolysed complex Pt en<sub>2</sub>(en-H)<sup>3+</sup>, a similar calculation has been performed for a few wavelengths (Table 3), where the change of both absorption and circular dichroism was appreciable and could be measured with some accuracy.

## DISCUSSION

Let us first compare the results of Nyman and Plane<sup>4</sup> and the ones reported here. Especially for the sulphate system, the situation is rather clear. It seems that the above-mentioned authors<sup>4</sup> used the concentration range  $0 < C_L < 0.1$  M. As pointed out above, the present measurements indicate that one has to consider the formation of the second sulphate complex also under these conditions. It is therefore probable that the stability constant  $\beta_{10}$  given by Nyman and Plane<sup>4</sup> is too low.<sup>6-9</sup> It is also interesting to note that the third complex begins to appear in the same concentration range as it does in the case of the Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> system.<sup>2</sup>

Considering the chloride system, it seems unreasonably that for such a highly charged ion as Pt en<sub>3</sub><sup>4+</sup> association products with only one chloride

ion, as suggested by Nyman and Plane, should exist, especially when the chloride concentration is raised to such high values as in this investigation. Also, a comparison with what has been found in the case of  $\text{Co}(\text{NH}_3)_6^{3+}$  system<sup>2</sup> suggests that the latter interpretation given above is the more realistic one. This should then mean that the increase of the circular dichroism coefficients for the successive chloride complexes is proportional to the increase of the corresponding extinction coefficients (eqn. 6).

In order to understand this we have to consider the nature of the mechanisms that infer a change of circular dichroism of dihedral complexes when engaged in outer-sphere complexes.

As pointed out above, the CD peak at about 260 nm must correspond to the first ligand field transition. In the  $D_3$  symmetry this transition will be split into two components of  $E$  and  $A_2$  symmetry, the rotational strengths being of opposite signs.<sup>17</sup> As there is no indication of a negative CD absorption in the close vicinity of this peak, one must assume that the trigonal splitting is rather small.

The observed CD peak then results from the almost complete cancellation between the  $E$  and  $A_2$  components of different sign. In order to tell which of the two components has the somewhat larger magnitude, we must know the absolute configuration of the  $(-)\text{-Pt en}_3^{4+}$  ion. As no X-ray analysis has yet been performed of this ion we have to rely on reasoning by analogy. The negative rotation at the sodium D line indicates that the ligand to metal charge transfer absorption must give a negative CD absorption in the far ultraviolet. By analogy with, *e.g.*, the  $(+)\text{-Co en}_3^{3+}$  that also has a negative charge transfer CD band<sup>18</sup> and the absolute configuration of which is known,<sup>19</sup> one can infer that the  $(-)\text{-Pt en}_3^{4+}$  has a  $\Delta$ <sup>20</sup> (or  $M(C_3)$ <sup>21</sup>) configuration. Then from Mason's criterion<sup>22</sup> for the absolute configuration of dihedral complexes, the CD component of  $E$  symmetry of the first ligand field transition must have a positive sign. That is, what we observe is the positive difference between the circular dichroism of the  $E$  and  $A_2$  transitions.

This knowledge enables us to discuss the various mechanisms that may affect the changes of the CD spectrum when outer-sphere ligands are attached to the  $(-)\text{-Pt en}_3^{4+}$  ion.

For the first sulphate complex a model analogous to the  $\text{Co en}_3^{3+} - \text{PO}_4^{3-}$  ion pair discussed by Mason and Norman<sup>3</sup> can be used: The charge transfer transition, being of  $E$  symmetry, can mix with the  $E$  components of the first and second ligand-field transitions  $E_a$  and  $E_b$ , respectively. This results in part of the magnetic moment of the  $E_a$  transition being borrowed from and shared with  $E_b$  and charge transfer transitions, decreasing the rotational strength,  $R_E$ , of the first ligand field band and increasing that,  $R_{E_b}$ , of the second one. This second ligand field transition is magnetically forbidden as it is of  $T_{2g}$  symmetry in  $O_h$ . It owes its rotational strength to similar interaction between the  $E_b$  and the  $E_a$  states also in the undisturbed dihedral complex. As the separation between the two ligand field transitions, judged from the CD-spectrum (Fig. 3) is only about  $3000 \text{ cm}^{-1}$ , this coupling must be very pronounced which explains the six times greater magnitude of  $R_{E_b}$  compared to that of the  $\text{Co en}_3^{3+}$  analogue, where the corresponding separation is about  $8000 \text{ cm}^{-1}$ .

The main point of the argument, however, lies in the decrease of  $R_{E_a}$ . Hence, we should expect a decrease also of the sum  $R_{E_a} + R_A$ , and, consequently, of the observed circular dichroism.

From the observations made of a number of  $\text{Co en}_3^{3+}$  outer-sphere complexes Mason and coworkers<sup>16</sup> have suggested that for complexes containing an even number of outer-sphere ligands the charge transfer transition most probably has components of both  $E$  and  $A_2$  symmetry. Hence both  $R_{E_a}$  and  $R_A$ , of the first ligand field transition will decrease due to loss of magnetic moment and the CD spectrum of such outer-sphere complexes will appear similar to that of the free central group. For complexes with an odd number of outer-sphere ligands, on the other hand, the situation seems to be very much similar to what has been discussed above for the first outer-sphere complex.

Turning now to the experimental results, the steady increase of the function  $\rho$  for small values of  $\text{SO}_4^{2-}$  indicated that, for the three wavelengths investigated, the values of  $\Delta_1$  are less than those of  $\Delta_2$ . This is in accordance with the theory given above. Furthermore, the smallest  $\Delta_1$  value is found for 270 nm, where the  $E_a$  component should be the dominating one in consequence of the adopted configurational criterion. Also in favour of the quoted theory is the fact that  $\Delta_3$  seems to be smaller than  $\Delta_2$ , at least for the wavelength 270 nm.

However, apart from this mechanism of dissipation of the magnetic moment originating from the magnetically allowed  $T_{1g}$  transition (in the  $O_h$  point group), there must be another one responsible for the general increase of the rotational strength compared to that of the free central group. A guide to this mechanism seems to be the fact that there is a much greater increase of the absorption of unpolarised light in the spectral range of ligand field transitions, when sulphate ions are added to  $\text{Pt en}_3^{4+}$  (Fig. 2), than there is in the case of the  $\text{Co(III)}$  analogue. This probably means that the mixing of the outer-sphere ligand states with the ligand field states is much stronger in the  $\text{Pt(IV)}$  case than in the  $\text{Co(III)}$  one, hence giving rise to a pronounced increase of the dipole strength of the originally Laporte-forbidden  $d-d$  transitions in the  $\text{Pt en}_3^{4+}$  ion.

Consequently, the rotational strengths of both the  $E$  and  $A_2$  transitions should increase. If this increase is proportional to the magnitudes of the respective rotational strengths of the free central ion, there should then be a resulting increase of the observable CD band. This explanation is then very similar to the one<sup>23</sup> claimed as an explanation of the induction of circular dichroism of the first ligand field transition of  $\text{Co(NH}_3)_6^{3+}$  by an optically active agent.

It then follows that the two mechanisms mentioned above may combine to give the effects observed for the  $\text{Pt en}_3^{4+}-\text{SO}_4^{2-}$  system. Turning then to the chloride system, the second mechanism seems to offer an acceptable explanation of the effects observed. It gives us the requested relation between the increase of circular dichroism and light absorption coefficients. Strictly speaking, the increase of the rotational strength should be proportional to the square root of the increase of the dipole strength<sup>24</sup> and not directly proportional as our criterion above (eqn. 6) requests. However, for one thing, we have taken into consideration only the CD and extinction coefficients instead of

the integrated areas under the peaks. Again, it is difficult to say how much of the increase of the light absorption that arises from the low frequency tail of the absorption band due to the charge transfer from the chloride ions to the central group, and how much that can be ascribed to an increase of the  $d-d$  transition band intensity.

Let us then turn to the protolysed complex  $\text{Pt en}_2(\text{en-H})^{3+}$  and the changes of absorption and CD spectrum brought about by outer-sphere coordination. The most obvious characteristic of this ion is the shift of first spin-allowed ligand field transition from about 260 nm in  $\text{Pt en}_3^{4+}$  to about 300 nm in  $\text{Pt en}_2(\text{en-H})^{3+}$ . This and similar shifts for other ammine complexes of Pt(IV) are probably caused by a decrease in the value of  $10 Dq$ , the ligand field splitting parameter. Such a decrease is expected (*cf.* Ref. 25, p. 37) for a  $\pi$ -bonding interaction between the lone pair of the nitrogen that has lost its proton and the  $t_{2g}$  orbitals of the metal atom.

It may also be noted (*cf.*, *e.g.*, Fig. 5) that the intensity of the shifted band is considerably increased. This may be due to the mixing of the even metal orbitals with the odd nitrogen  $2p$  orbital, thus giving the transition to some part an odd-even character.

The interesting fact now emerges that whereas chloride ions shift the position of maximum absorption and maximum CD towards longer wavelengths, the contrary holds for thiosulphate ions. Obviously, different mechanisms must be suggested as an explanation. It could be argued, though, that the effect of thiosulphate ions was to decrease the above mentioned  $N(2p)-t_{2g}$  interaction and that the chloride ions should increase it. Then, however, the intensity ought to follow the same trend, *i.e.* it should be decreased in the thiosulphate system and increased in the chloride system. Inspection of Fig. 5 shows that this is not the case.

In this situation the present author should like to suggest that the bonding mechanism in the case of the thiosulphate system is the one called "mechanism a" in Ref. 10 and schematically illustrated in Fig. 9a. It implies a — weak — interaction between suitable, filled orbitals of the outer-sphere ligand and the antibonding  $e_g^*$  orbitals of the central group. This should raise the empty orbital to which the electron from the  $t_{2g}$  level is lifted in the ligand field transition resulting in a blue-shift of the absorption maximum. This last transition can also borrow some intensity from the charge-transfer transition associated with this orbital scheme. *I.e.* this is the same argument that was put forward above to explain the increase of the  $d-d$  transitions of  $\text{Pt en}_3^{4+}$  in chloride and sulphate media. In these cases, however, it is not possible to

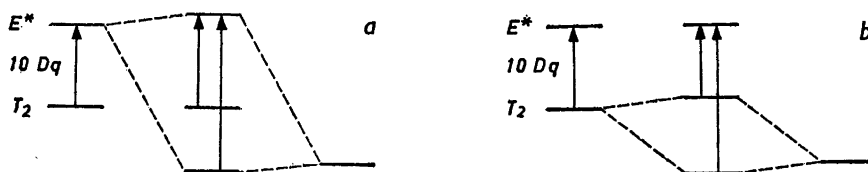


Fig. 9. Tentative MO-bonding schemes for the interaction between platinum orbitals (extreme left) and outer-sphere ligand orbitals (extreme right). The arrows in the middle indicate the  $d-d$ -transition (left) and the charge-transfer transition (right).

analyse any shifts of the almost nonresolvable absorption curves for these systems.

For the chloride case, another type of interaction is suggested, *viz.*, the one schematically given in Fig. 9b. This implies an interaction between suitable, filled orbitals of the ligand and the  $t_{2g}$  orbitals of the central group. Thus, it has a formal similarity to the  $\pi$ -bonding in the first coordination sphere and results in a similar decrease of  $10 Dq$ .

The question then arises, how many thiosulfato and chloro outer-sphere complexes that may exist. For the chloride system the changes are so small that they are not possible to analyse. The thiosulphate system shows a pattern (Table 3) similar to that of the  $\text{Pt en}_3^{4+}-\text{Cl}^-$  system (Table 2). Thus one or possibly several outer-sphere complexes exist. Some observations favour the second interpretation. One of these is the shoulder at about 265 nm of the absorption spectrum (Fig. 5), which indicates the presence of a new species when the thiosulphate concentration is sufficiently increased. Connected with this interpretation is the decrease of the function  $\rho$ , formed not from  $\Delta$  and  $\epsilon$  values of the same wavelengths, but from  $\Delta$  values at a wavelength where the CD could be measured easily and from  $\epsilon$  values at a wavelength (270 nm) close to the above-mentioned shoulder. Apart from probable small variations of the refractive index effect, nothing in the deductions from eqn. (5) is changed by this procedure.

Another observation that may be made from the presented data is the existence of a concentration range  $0.25 \text{ M} < C_L < 0.7 \text{ M}$  of almost constant  $\Delta$  (Fig. 8). For the highest  $C_L$  an increase of  $\Delta$  is again noted. Although the experimental information is rather scarce, it may be worth pointing out that this range of constancy of  $\Delta$  is the one where the formation of a second complex — judged from the shoulder of the absorption maximum — sets in. One may therefore propose the tentative interpretation that for the first two complexes,  $\Delta_1$  and  $\Delta_2$  are about the same whereas they are distinguished by their absorption spectra. The question whether the increase of  $\Delta$  for great  $C_L$  should indicate the presence of a third complex is premature.

To sum up, it seems that the outer-sphere systems of  $\text{Pt en}_3^{4+}$  and its corresponding base are more complicated and yield stronger complexes than what has hitherto<sup>4-5</sup> been assumed. However, as the present interpretations — but for that of the  $\text{Pt en}_3^{4+}-\text{SO}_4^{2-}$  system — are of an indirect character, there is still a need for the application of direct analysis based on thermodynamic methods.

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