Studies on Five-co-ordinate d^8 Metal Ions. Part 3.* Stability Constants for the Reversible Formation of Five-co-ordinate Complexes from the Bis(2,2′-bipyridine)- and Bis(1,10-phenanthroline)-platinum(II) Cations

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The dipositive ions bis(1,10-phenanthroline)platinum(II) and bis(2,2′-bipyridine)platinum(II) both add nucleophiles reversibly in aqueous solution giving five-co-ordinate products. The stability constants for complex formation with 12 different nucleophiles (Nu) have been determined at 23.0 ± 0.5 °C. It has been shown that the stability constants for the phenanthroline (K_{phen}) and the bipyridine (K_{bipy}) complexes correlate according to the expression $\log_{10} K_{\text{phen}} = 1.01 (\log_{10} K_{\text{bipy}}) - 1.21$. These series of stability constants were compared with rate and stability data from the literature; the values correlate only with the equilibrium constants for the reaction $[PtCl_2(C_2H_4)(H_2O)] + Nu \rightleftharpoons [PtCl_2(C_2H_4)(Nu)] + H_2O$. In all cases a slow substitution reaction followed the rapid equilibrium. This substitution was faster for the bipyridine complexes than for the phenanthroline complexes.

The investigation of reactions of platinum(II) has played a crucial role in the development of co-ordination chemistry.[1-4] Despite the great interest in the reaction mechanisms of platinum(II) substitution reactions, leading to a large number of kinetic investigations,[1,2] very little data are available describing the equilibrium thermodynamics for Pt^{II} complexes even though they have a major significance for mechanistic studies. One obvious reason for this is the difficulty of finding well defined and rapid reactions which can proceed to equilibrium without interference from parallel or consecutive processes.

Chatt and co-workers[5,6] took advantage of the large *trans* effect of ethene, which makes reaction (1)† fast enough to reach

$$[PtCl_2(C_2H_4)(H_2O)] + Nu \rightleftharpoons [PtCl_2(C_2H_4)(Nu)] + H_2O \quad (1)$$

equilibrium without significant interference from other reactions. By using this system, it was possible to determine the formation constants for a series of nucleophiles including amines, halide ions, SCN^-, and OH^-. Later work, based on similar principles, has been performed but has been limited to closely related groups of nucleophiles such as amines[7,8] or alkenes.[9] Most recently, systematic studies of equilibria based on rate measurements have been performed.[10,11] This approach permits accurate measurements on one single reaction in a sequence of parallel and consecutive steps where equilibrium with respect to one specific reaction cannot be obtained. This method is highly reliable, but also laborious, and only data for reactions involving SCN^- and halide ions have appeared.

Potentiometric measurements based on the redox equilibria between a platinum electrode and aqueous solutions of platinum complexes have also been published.[12,13] However, since the platinum complexes are inert, the electrode reactions are likely to be slow, and electrode kinetic studies confirm this.[14] For this reason, it is difficult to obtain equilibrium with respect to one particular reaction and data based on potentiometric measurements alone may not be very accurate.

Recently, we showed that the ion $[Pt(phen)_2]^{2+}$‡ rapidly adds cyanide in aqueous solution, forming the compound $[Pt(phen)_2(CN)]^+$, which is five-co-ordinate both in solution and in the solid state.[15] This five-co-ordinate ion was also shown to be substitutionally inert,[16] and the solution n.m.r. spectra show phen resonances (which are equivalent on the n.m.r. time-scale) with ^{195}Pt–^{13}C coupling constants of approximately the same magnitude as found in $[Pt(phen)_2]^{2+}$. From these data it was concluded that the description of compounds of this type as containing 'half-bonded' phen[17] is inadequate. Since the bipy molecule is not rigid (unlike the phen molecule), one of the pyridine rings in a singly bonded bipy ligand may be free to rotate, and it might be anticipated that a reaction between $[Pt(bipy)_2]^{2+}$ and CN^- might produce a classical four-co-ordinate complex with properties distinctly different from those of the analogous phen complex.

Thus, the aim of the present study has been to test whether this rapid cyanide addition represents one example of a general reaction type for both the $[Pt(phen)_2]^{2+}$ and the $[Pt(bipy)_2]^{2+}$ cations. For this purpose the reactions of the two complex ions with a series of nucleophiles have been studied spectrophotometrically, and the values of the equilibrium constants for the reactions with I^-, SO_3^{2-}, $S_2O_3^{2-}$, thiourea (tu), OH^-, NH_3, NH_2Me, $NHMe_2$, NMe_3, piperidine (pip), and 1,2-diaminoethane (en) have been measured. The amine systems have been studied in a medium containing $[NHR_3]_2[SO_4]$ (R = Me or H) so that protonation of the amine can be neglected. All other equilibria were measured in solution without addition of electrolyte assuming all activity coefficients to be unity within experimental error in the concentration range used ($< 10^{-3}$ mol dm^{-3}).

Experimental

Reagents.—$[Pt(phen)_2][NO_3]_2$ and $[Pt(phen)_2(CN)][NO_3]$ were prepared and characterised as described previously.[15] $[Pt(bipy)_2][ClO_4]_2$ was prepared according to published methods[18] and was characterized by u.v., i.r., and n.m.r. spectra which agreed with literature data[19,20] (Found: C, 36.6; H, 2.95; N, 12.3. Calc. for $C_{20}H_{20}N_6O_8Pt$: C, 36.0; H, 3.00; N, 12.6%). The $[NHR_3]_2[SO_4]$ salts were made from aqueous solutions of the amines (Fluka or Riedel de Haen, reagent grade) which were distilled and the vapour was condensed into ice-cooled 50% sulphuric acid (Merck, p.A.) until the mixture was alkaline. A

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* Part 2 is ref. 16.

† Throughout this paper a nucleophile is abbreviated as Nu. The charge of Nu must be taken into consideration when considering the charge of its complexes.

‡ The ligands 1,10-phenanthroline and 2,2′-bipyridine are abbreviated as phen and bipy, respectively, and collectively as L throughout this paper.

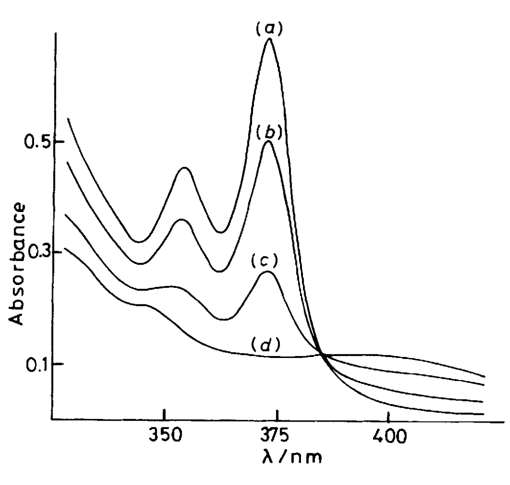

Figure 1. Electronic spectra of aqueous solutions containing 8.30×10^{-5} mol dm^{-3} $[Pt(phen)_2][NO_3]_2$ and the following concentrations of Na_2SO_3: (*a*) 0, (*b*) 1.96×10^{-5}, (*c*) 1.11×10^{-4}, (*d*) 1.96×10^{-4} mol dm^{-3}. All higher concentrations gave spectra identical to (*d*)

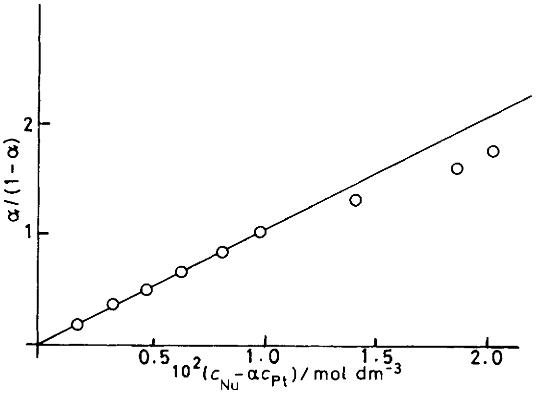

Figure 2. Plot of $\alpha/(1 - \alpha)$ *versus* $(c_{Nu} - \alpha c_{Pt})$ [see equation (3)] showing the 1:1 stoicheiometry of the reaction between $[Pt(phen)_2]^{2+}$ and NH_3 in aqueous 0.010 mol dm^{-3} $[NH_4]_2[SO_4]$. The values corresponding to $[NH_3] > 10^{-3}$ mol dm^{-3} show deviation from the line due to the slow reaction $[Pt(phen)_2(NH_3)]^{2+} + NH_3 \longrightarrow [Pt(phen)(NH_3)_2]^{2+}$ + phen. The concentration of the complex is 2.07×10^{-5} mol dm^{-3}

five-fold excess of propan-2-ol was added and the white precipitate of the sulphate was isolated by filtration and recrystallized from hot propan-2-ol, collected on the filter, washed with diethyl ether and dried in a vacuum desiccator.

The reactions between $[PtL_2]^{2+}$ and the amines were performed in solutions containing $[NHR_3]_2[SO_4]$ which were prepared by dissolving an accurately weighed amount of the sulphate salt (see above) and diluting to a known volume with distilled water. Solutions of amines were prepared by mixing solutions of $[NHR_3]_2[SO_4]$ with the appropriate volume of freshly prepared standard sodium hydroxide solution (Merck, Titrisol). This type of standard NaOH was also used for the measurements of the OH^- reactions. All other reagent solutions were prepared from AnalaR reagents which were used as received.

Measurements.—Electronic spectra of the solutions of the Pt complexes were recorded with a Cary 214 spectrophotometer in the range shown in Figure 1. For the spectrophotometric measurements on the mixtures of the complexes and the nucleophiles, the solutions were prepared by adding the ligand solution (25 μl) to $[PtL_2]^{2+}$ solution (2.50 cm^3) in the cuvette by means of an accurate micropipette. More (25 μl) of the solution of the nucleophile was added to the cuvette and the spectrum recorded again. For those reaction mixtures which were not stable during the time of recording of a series of spectra the calculations were made from absorbance values which were determined at a fixed wavelength (335 nm for the bipy complexes and 375 nm for the phen complexes). All the data for the calculations of the equilibrium concentrations were corrected for the volume change assuming all volumes to be additive. All the solutions were thermostatted at 23.0 ± 0.5 °C.

Results and Discussion

An example of the influence of addition of nucleophiles on the spectra of the complexes in aqueous solution is shown in Figure 1. Within experimental error, the observed reactions lead to the same types of spectral changes for each complex and the positions of the isosbestic points (278 nm and 383 nm for the phen complexes and 269 nm and 364 nm for the bipy complexes) are within ±2 nm irrespective of the nucleophile used. The only significant differences between the spectra in the $[Pt(phen)_2(Nu)]$ series are the positions of the broad and weak absorption bands at wavelengths >385 nm. A phenomenon similar to this is not observed in the spectra of the bipy complexes. These spectral changes are completed within the time of mixing.

Since the previously reported spectrum[15] of pure $[Pt(phen)_2(CN)][ClO_4]$ dissolved in water is essentially identical to the spectra of the $[Pt(phen)_2]^{2+}$ + Nu mixtures when the Nu is present in excess, these spectra may be taken as the spectra of pure $[Pt(phen)_2(Nu)]$. Following this assumption, the relative change in absorbance at a fixed wavelength is identical to the degree of conversion, α, of $[Pt(phen)_2]^{2+}$ into $[Pt(phen)_2(Nu)]$. The same assumption is made concerning the bipy complexes. Application of the law of mass action to the addition equilibrium (2) leads to the expression (3), where c_{Nu}

$$[PtL_2]^{2+} + Nu \rightleftharpoons [PtL_2(Nu)] \qquad (2)$$

$$\alpha/(1 - \alpha) = K(c_{Nu} - \alpha c_{Pt}) \qquad (3)$$

and c_{Pt} represent the total concentrations of the nucleophile and the platinum complex, respectively, and K is the equilibrium constant for reaction (2). Thus a 1:1 addition equilibrium will be confirmed by a linear relationship with an intercept of zero and a gradient of K when $\alpha/(1 - \alpha)$ is plotted against $c_{Nu} - \alpha c_{Pt}$. A typical plot of this type using the data for the reaction between $[Pt(phen)_2]^{2+}$ and NH_3 is shown in Figure 2, and it is seen that for $\alpha < 0.6$ a linear correlation in accordance with equation (3) is valid. This confirms that the reaction rapidly goes to an equilibrium with the stoicheiometry corresponding to equation (2).

When the equilibrium mixture contains the nucleophile in an excess the rapid, initial spectral changes are followed by slower changes due to the substitution reaction (4) which has

$$[PtL_2(Nu)] + Nu \longrightarrow [PtL(Nu)_2] + L \qquad (4)$$

previously been reported[16] for the reaction where L = phen and Nu = CN^-. This reaction was always observed to be faster for the bipy than for the phen complexes, which is in agreement with the general observation that the non-rigid bipy ligand is a better leaving group than phen.[3,4] However, only for ligands which have a low affinity *and* possess a high nucleophilicity did this affect the determination of K. Thus, for the reaction where L = bipy and Nu = en, this type of measurement could not be

Table 1. Equilibrium data for reaction (2) in aqueous solution at 23.0 ± 0.5 °C

L	Nu	$[PtL_2^{2+}]$/ mol dm^{-3}	Range of [Nu]/ mol dm^{-3}	No. of runs	Electrolyte concentration[a]/mol dm^{-3}	$\log_{10} K$
bipy	I^-	1.70×10^{-5}—3.41×10^{-5}	1.49×10^{-4}—1.11×10^{-3}	9		2.6 ∓ 0.3
	SO_3^{2-}	1.2×10^{-5}	9.9×10^{-6}—2.9×10^{-5} [b]	3		6.0 ∓ 0.2
	$S_2O_3^{2-}$	4.77×10^{-6}	1.98×10^{-7}—3.05×10^{-6}	11		6.7 ∓ 0.2
	tu	3.43×10^{-5}	1.96×10^{-5}—1.38×10^{-4}	5		4.13 ∓ 0.05
	OH^-	1.44×10^{-6}	4.74×10^{-3}—8.33×10^{-4}	9		4.11 ∓ 0.03 [c]
	NH_3	3.41×10^{-5}	1.74×10^{-3}—8.35×10^{-4}	4	0.010	3.32 ∓ 0.04
	NH_2Me	3.44×10^{-5}	0.99×10^{-3}—8.26×10^{-3}	5	0.010	3.18 ∓ 0.03
	$NHMe_2$	3.44×10^{-5}	1.98×10^{-4}—2.91×10^{-3}	8	0.010	3.02 ∓ 0.07
	NMe_3	3.47×10^{-5}	0.020—0.165	6	0.20	0.020 ∓ 0.02
	pip	3.44×10^{-5}	1.98×10^{-3}—0.0222	10	0.010	3.65 ∓ 0.05
phen	I^-	1.36×10^{-5}	7.4×10^{-3}—4.03×10^{-2}	6		0.85 ∓ 0.15
	SO_3^{2-}	8.22×10^{-5}	8.7×10^{-6}—8.71×10^{-5} [b]	6		4.74 ∓ 0.1
	$S_2O_3^{2-}$	$(8.2$—$16.1) \times 10^{-5}$	3.9×10^{-6}—7.4×10^{-5}	11		6.4 ∓ 0.1
	tu	2.0×10^{-5}	1.96×10^{-5}—4.67×10^{-4}	4		3.15 ∓ 0.04
	OH^-	1.29×10^{-5}	4.95×10^{-5}—0.0121	12		2.60 ∓ 0.02
	NH_3	1.36×10^{-5}	1.74×10^{-3}—0.0242	6	0.010	2.02 ∓ 0.02
	NH_2Me	1.35×10^{-5}	1.98×10^{-3}—0.0371	7	0.010	2.43 ∓ 0.03
	$NHMe_2$	1.35×10^{-5}	1.98×10^{-3}—0.0333	10	0.010	1.60 ∓ 0.05
	NMe_3	1.06×10^{-5}	0.020—0.276	5	0.20	-0.32 ∓ 0.10
	en	1.21×10^{-5}	1.98×10^{-3}—0.0319	8	0.010	0.88 ∓ 0.01
	pip	1.26×10^{-5}	1.98×10^{-3}—0.0519	8	0.010	1.63 ∓ 0.03

[a] The concentration of $[NHR_3]_2[SO_4]$ corresponding to the amine used in the experiment. The reactions with the other nucleophiles were measured in water without addition of electrolyte. [b] The values for the equilibrium concentrations of SO_3^{2-} were calculated from the formal concentration and corrected for protonation using a pK_a value of 7.20 for the HSO_3^- ion. The data gave no evidence for any significant reaction between the Pt complexes and HSO_3^- or $S_2O_5^{2-}$ in the concentration range used. [c] Despite many attempts we were unable to reproduce the value of 5.0 given by ref. 18.

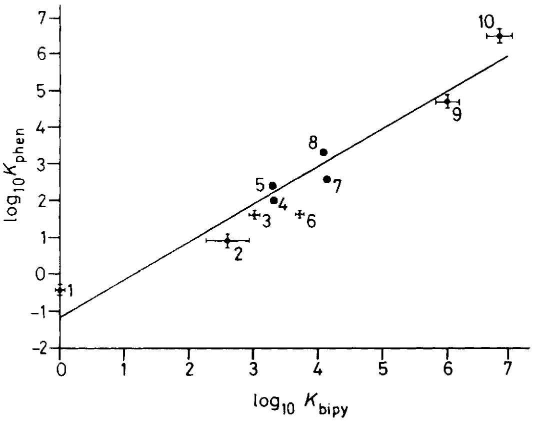

Figure 3. Plot of $\log_{10} K_{phen}$ *versus* $\log_{10} K_{bipy}$ as defined in equation (5). The numbers refer to the equilibria with the following nucleophiles: (1) NMe_3, (2) I^-, (3) $NHMe_2$, (4) NH_3, (5) NH_2Me, (6) pip, (7) tu, (8) OH^-, (9) SO_3^{2-}, (10) $S_2O_3^{2-}$

made since the spectral changes due to reaction (2) were only observable at en concentrations at which the reaction (4) was significant. Similar factors precluded the determination of K for the reactions with SCN^- or Br^-, and the reported values for Nu = I^- are associated with a considerable error. It is, however evident from the experiments that the K values for the Br^- and SCN^- reactions are *lower* than the values for the I^- equilibrium.

The spectra of the reaction mixtures with cyanide and triphenylphosphine (the latter in methanol solution) showed only a quantitative reaction and a calculation of K was not possible from these data. By considering the errors in the measurements this leads to a lower limit for K of 10^8 dm^3 mol^{-1} for both these systems.

For the ligands pyridine (py), bipy, N_3^-, Cl^-, CH_2CHCH_2OH (all measured in concentrations < *ca.* 10^{-2} mol dm^{-3}) and C_2H_4 and CO [saturated solution at 1 atm (*ca.* 10^5Pa)] no reaction was observed and for these systems it may be concluded that the stability constants are lower than *ca.* 0.2 dm^3 mol^{-1}.

The results for the systems with K values for equilibrium (2) which are within the range of the experiment are given in Table 1, together with some experimental details. Figure 3 shows that the K values for the equilibrium (2) where L = phen (K_{phen}) correlate with the equilibrium constants for the reactions with L = bipy (K_{bipy}) according to the expression (5). This close

$$\log_{10} K_{phen} = 1.01(\log_{10} K_{bipy}) - 1.21 \qquad (5)$$

relationship between the phen system and the bipy system together with the fact that both react in rapid, reversible processes indicate that species of similar type are being formed in all the reactions. Table 2 shows the data for the $[Pt(phen)_2]^{2+}$ reactions together with rate and equilibrium data for other reactions involving the same nucleophiles.

It is seen that even for closely related systems like the amine series no obvious correlation with the basicity of the ligands exists. Tobe and co-workers[7,8] observed a linear correlation between $\log_{10}K$ and pK_a with a slope of 0.57 over a range of $\leqslant 6$ pH units for a series of amines (am) undergoing reaction (6)

$$[PtCl_3(dmso)]^- + am \rightleftharpoons trans\text{-}[PtCl_2(am)(dmso)] + Cl^- \qquad (6)$$

(dmso = dimethyl sulphoxide). Though the precisions of the measurements are of the same magnitude, the range of pK values in the present work is small and a similar correlation is not obvious. It is, however, significant that for NMe_3 K_{phen} and K_{bipy} are much lower than the K values for the other amine systems despite the pK_a values for all the amines being of similar

Table 2. Equilibrium constants and nucleophilic reactivity constants (n^0_{Pt}) for a series of nucleophiles

Nu	$\log_{10} K_{phen}$ [a]	n^0_{Pt} [b]	$\log_{10} K_Z$ [c,d]	$\log_{10} K_{Hg}$ [e]	pK_a [f]
CO	< -0.7				
C_2H_4	< -0.7				
CH_2CHCH_2OH	< -0.7				
bipy	< -0.7				3.62[g]
Cl^-	< -0.7	3.04	2.52	5.25	-6
py	< -0.7	3.13			5.2
N_3^-	< -0.7	3.58			4.7
Br^-	$\leqslant -0.7$	4.18	3.04	6.62	-8
SCN^-	$\leqslant -0.7$	6.65	>4.6	6.05	<0
NMe_3	-0.42		5.5		9.89
I^-	0.85	5.42	4.60	8.60	-10
en	0.88			8.25	10.05
$NHMe_2$	1.60		8.0		10.86
pip	1.63		8.2		11.07
NH_3	2.02	3.06	7.8	7.60	9.25
NH_2Me	2.43		8.6		10.75
OH^-	2.60	<3[h]	9	9.32	15.7
tu	3.15	7.17			$\leqslant -1$
SO_3^{2-}	4.74	5.79		8.11	6.9
$S_2O_3^{2-}$	6.4	7.34		10.90	<0
PPh_3	>8			>10[h]	$\leqslant 0$
CN^-	>8	7.0		14.1	9.1

[a] Data from Table 1. [b] Nucleophilic reactivity constants defined as the logarithm of the rate of the reaction *trans*-$[Pt(py)_2Cl_2] + Nu \rightleftharpoons$ *trans*-$[Pt(py)_2Cl(Nu)] + Cl^-$ relative to the rate of reaction when Nu = MeOH (see ref. 3). [c] Equilibrium constants for reaction (1) in aqueous KNO_3 (0.2 mol dm^{-3}) at 23 °C (refs. 5 and 6). [d] These data have been quoted in ref. 3, but this text apparently contains two misprints: the equilibrium data for OH^-, NH_3, and the other amines should be referred to the reaction $[PtCl_2(C_2H_4)(H_2O)] + Nu \rightleftharpoons [PtCl_2(C_2H_4)(Nu)] + H_2O$ and the K value for the process where Nu = OH^- should be 10^9 according to the original references (5 and 6). [e] Equilibrium constants for reaction (7), aqueous KNO_3 (0.1 mol dm^{-3}) at 20 °C (G. Schwarzenbach and M. Schellenberg, *Helv. Chim. Acta*, 1963, **1**, 28). [f] Data from refs. 3—6. [g] From B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 1961, 2007. [h] Estimated limit.

magnitude. This effect was also observed by Chatt and co-workers[5,6] for reaction (1) [see the $\log_{10} K_Z$ values for reaction (1) in Table 2] who attributed this to the steric effects from the bulky Me groups bonded to the donor atom. Apart from the results for the NMe_3 systems, it is seen that the data for $\log_{10} K_Z$ and $\log_{10} K_{phen}$ show a remarkably good correlation, confirming the relative affinities for halogens, amines, and hydroxide reported in ref. 6.

It is also seen from Table 2 that the equilibrium data ($\log_{10} K_{phen}$) for reaction (2) roughly parallel the $\log_{10} K_{Hg}$ values for reaction (7). The most characteristic difference is that

$$HgMe^+ + Nu \rightleftharpoons HgMe(Nu) \qquad (7)$$

compared to platinum, mercury shows a greater affinity for hydroxide and for the halides than for the amines.

A comparison between $\log_{10} K_{phen}$ and the nucleophilicity, n^0_{Pt} (defined in Table 2) shows no obvious correlation although both describe properties of five-co-ordinate systems. However, affinity reflects the ground-state properties whereas the nucleophilicity refers to transition state and the results show that the ground-state properties of the four- and five-co-ordinated systems parallel each other. Also, the order of affinity does not parallel the relative positions of the ligands in the *trans* effect series.[1–4] Ligands like CO and alkenes have a *trans* effect similar to that of CN^- and phosphines, but clearly the former pair show affinities for platinum(II) which are many orders of magnitude lower. The low stability of alkenes has also been observed by Denning and Venanzi[9] who showed the affinities for Pt^{II} of a series of alkene derivatives to be of the same order of magnitude as Br^- and I^-. It is therefore to be expected that they fall outside the range covered by the procedure used in this work.

It is of interest to observe the values of K_{phen} for the reactions of the bidentate ligands bipy and en. Whereas the former shows no reaction the latter shows an affinity which is lower than all the other amines used (except NMe_3). Both bipy and en will normally form much stronger complexes than py and unidentate amines because of the chelate effect but clearly do not show these properties in the present case. These observations indicate that species with co-ordination numbers higher than five are not formed. It is, however, evident that the compounds $[PtL_2(en)]^{2+}$ show a remarkable instability. This can be attributed to the well known kinetic neighbouring-group *effect*[4] of the non-bonded amino group which acts as a very strong nucleophile displacing bipy and forming $[Pt(bipy)(en)]^{2+}$. Although slow compared to the rate of formation of the five-co-ordinate species, this reaction is fast enough to obstruct the spectrophotometric determination of the stability constant for the formation of $[Pt(bipy)_2(en)]^{2+}$.

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