Displacement of Ammonia from Planar Four-co-ordinate Platinum(II) Complexes by Cyanide. The Existence of a Strong *cis*-Labilising Effect by CN^-

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The reactions of $[Pt(NH_3)_4]^{2+}$, *cis*- and *trans*-$[Pt(NH_3)_2(CN)_2]$, *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$, and $[Pt(NH_3)Cl_3]^-$ with CN^- in basic aqueous solution have been studied. In all cases the final product is the $[Pt(CN)_4]^{2-}$ ion but where hydroxo species are produced as intermediates the final conversion can be very slow. While the displacement of the first ammonia from $[Pt(NH_3)_4]^{2+}$ is rate limiting, many of the other species react in an observable stepwise fashion. The individual stages have been characterised and examined. The similarity of the rate constants for the displacement of NH_3 from the *cis*- and *trans*-$[Pt(NH_3)_2(CN)_2]$ isomers suggests that, at least in the reaction with CN^-, the *cis* effect of CN^- is comparable to its *trans* effect. Possible explanations are discussed.

In the course of a study of the displacement of cyclobutane-1,1′-dicarboxylate from Carboplatin [diammine(cyclobutane-1,1′-dicarboxylato)platinum(II)][1] we found that, while the chelate was readily displaced in acidic solution, in the presence or absence of chloride the reaction in neutral solution was very slow. While Cl^- yielded the expected product, *cis*-$[Pt(NH_3)_2Cl_2]$, we were unable to account for the spectral changes in the presence of stronger nucleophiles in terms of a simple displacement of the chelate. As part of our attempt to resolve this problem we examined the reaction with CN^- and observed that, after some initial disturbance, there was a smooth change of spectrum to one that was similar to, but not identical with, that of an authentic sample of $[Pt(CN)_4]^{2-}$. In order to decide whether the chelate was displaced before or after the ammonia we examined the analogous reactions of *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ and it soon became clear that this system was more complicated than might have been predicted from current views of nucleophilicity, lability and *cis* and *trans* effects and warranted a detailed examination.

The cyanide ion is known to be a strong nucleophile towards four-co-ordinate planar platinum(II) complexes with an $n_{Pt}{}^0$ value of 7.14.[2,3] There has been little systematic work on nucleophilic substitution by cyanide since then and much of this has been concerned with relatively inert substrates,[4–7] the displacement of a relatively labile ligand such as Cl^- often requiring fast reaction techniques. The use of CN^- to remove platinum from biological materials and/or co-ordinating polymers has received considerable attention.[8,9]

In contrast to the lability of co-ordinated chloride, nitrogen donors are usually relatively inert ligands. For example, both chlorides in *trans*-$[Pt(PEt_3)(pip)Cl_2]$ can be displaced by a range of nucleophiles while the piperidine (pip) remains bound in spite of being *trans* to the strongly labilising phosphine.[10] There are many studies of the displacement of amines under the *trans* effect of suitable ligands, usually facilitated by the addition of acid to protonate the amine and prevent the reverse reaction or else by the addition of hydroxide to fix the vacant co-ordination site.[11–17] In order to study the *trans* effect of cyanide in more detail and also to examine its *cis* effect, which has not previously been examined, we have studied the kinetics of the replacement of ammonia by cyanide in a number of related ammine complexes of platinum(II). The results are presented and discussed in this paper and a similar study of the displacement of primary amines and heterocyclic bases is complete and will be presented elsewhere.

Experimental

Materials.—Dipotassium tetrachloroplatinate(II) was prepared from metallic platinum by standard literature methods. The inorganic salts and the solvents were reagent-grade products.

Preparations.—The complexes *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ were prepared by the method of Kauffman and Cowan.[18]

Trans-Diamminedicyanoplatinum(II) was prepared by modifications of the methods of Chernyaev *et al.*[19] and Estaf'eva *et al.*[20] Silver nitrate (0.5662 g, 3.33 mmol) was added to a suspension of *trans*-$[Pt(NH_3)_2Cl_2]$ (0.5000 g, 1.67 mmol) in water (5 cm^3) and the mixture was stirred in the dark overnight. The white precipitate of AgCl was filtered off, washed three times with a few drops of water and the washings were combined with the greenish yellow filtrate. The solution was cooled in an ice-bath and then treated with dry potassium cyanide (0.0427 g, 3.33 mmol) and stirred. The acicular white crystals that separated were filtered off, washed with ethanol and diethyl ether and dried. Yield = 0.3 g (60%). The product was recrystallised from the minimum amount of boiling water (Found: C, 8.75; H, 2.10; N, 19.9; Pt, 69.3. $C_2H_6N_4Pt$ requires C, 8.55; H, 2.15; N, 19.9; Pt, 69.4%). IR: ν(C–N) 2119 cm^{-1} (lit.,[21] 2112 cm^{-1}).

cis-Diamminedicyanoplatinum(II) was prepared according to the method of Avshu and Parkins.[21] Polymeric $Pt(CN)_2$, prepared by boiling a solution of $K_2[Pt(CN)_4]$ with an equimolar amount of *cis*- or *trans*-$[Pt(NH_3)_2Cl_2]$, was treated with concentrated aqueous ammonia to give *cis*-$[Pt(NH_3)_2(CN)_2]$ (Found: C, 8.65; H, 2.05; N, 20.3. $C_2H_6N_4Pt$ requires C, 8.55; H, 2.15; N, 19.9%). IR: ν(C–N) 2118 and 2132 cm^{-1}.

The complex *trans*-$[Pt(NH_3)_2(OH)_2]$ was prepared in solution by adding silver nitrate (0.5662 g, 3.33 mmol) to a suspension of *trans*-$[Pt(NH_3)_2Cl_2]$ (0.500 g, 1.647 mmol) in water (5 cm^3) and shaking the mixture in the dark overnight. The white precipitate of silver chloride was filtered off, washed three times with a few drops of water and the combined washings and filtrate were brought to pH 8 by adding aqueous KOH (0.1 mol dm^{-3}) drop by drop.

Potassium triamminechloroplatinate(II) was prepared by the method of Elleman *et al.*[22] The complex *cis*-$[Pt(NH_3)_2Cl_2]$ (0.500 g, 1.67 mmol) was refluxed for 2 h with concentrated hydrochloric acid (100 cm^3) in the presence of some metallic platinum as catalyst. The mixture was cooled and the unreacted *cis*-$[Pt(NH_3)_2Cl_2]$ and the platinum were filtered off. The complex $[Pt(NH_3)_4]Cl_2$ (0.279 g, 0.833 mmol) was added to the stirred filtrate and the bright yellow $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$ precipitated was filtered off and washed with several portions of water. The crystals were suspended in water (40 cm^3) and an aqueous solution of $K_2[PtCl_4]$ (0.376 g, 0.833 mmol) was added to the swirled mixture. The green Magnus salt $[Pt(NH_3)_4][PtCl_4]$ that formed was filtered off and the filtrate evaporated to dryness under reduced pressure. The residue was recrystallised from the minimum amount of boiling water (Found: H, 0.90; Cl, 29.85; N, 3.80. H_3Cl_3KNPt requires H, 0.85; Cl, 29.75; N, 3.90%).

Tetraammineplatinum(II) chloride was prepared by the method of Keller.[23] Concentrated ammonia (2.5 cm^3) was added to a boiling, magnetically stirred, solution of $K_2[PtCl_4]$ (0.50 g, 1.1 mmol) in water (50 cm^3) and the stirring was continued for 10 min until the colour changed from red to pale yellow and there was only a faint smell of ammonia. The solution was cooled and stirred and a solution of $K_2[PtCl_4]$ (0.50 g, 1.1 mmol) in water (50 cm^3) was added slowly to precipitate the Magnus salt. This was filtered off, washed with several portions of hot water, dissolved in boiling concentrated aqueous ammonia and the solution evaporated to a volume of 20 cm^3. The solution was cooled and acetone–ethanol (1:1, 300 cm^3) was added quickly to the vigorously stirred solution. The white precipitate of $[Pt(NH_3)_4]Cl_2$ was filtered off, washed with ethanol and then acetone and air dried (Found: H, 3.55; Cl, 21.20; N, 16.70. $H_{12}Cl_2N_4Pt$ requires H, 3.60; Cl, 21.20; N, 16.75%).

Kinetics.—The reactions were initiated by mixing a known volume of an aqueous solution of the reagents (KCN, NaOH and $NaClO_4$) with a freshly prepared one of the complex, each of which had previously been brought to the reaction temperature. There was always at least a twenty-fold molar excess of CN$^-$ over complex in order to ensure first-order kinetics. The mixture was placed in the constant-temperature cell compartment of a Perkin Elmer Lambda 5 spectrophotometer and the absorbance changes were monitored, either as repetitive spectral changes over the wavelength range 220–300 nm, or, for the faster reactions, as a plot of absorbance, A_t, *versus* time, t, at a suitable wavelength. When there was no subsequent disturbance the first-order rate constants, k_{obs}, were determined from the slope of a plot of $\ln|A_\infty - A_t|$ against time, where A_∞ is the absorbance after six half-lives. In most cases the rate constant was determined by an iterative non-linear least-squares program that determined the values of k_{obs}, A_0 and A_∞ which best fit the A_t *versus* t data by use of the first-order rate expression, $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$. For two-stage processes a five-parameter (A_0, A_i, A_∞, k'_{obs}, k''_{obs}) Gauss–Newton algorithm non-linear regression was used to fit the A_t *versus* t data by the expression (1), A_i is the absorbance of the intermediate.

$$A_t = A_\infty + (A_0 - A_\infty)\exp(-k'_{obs}t) + k'_{obs}(A_i - A_\infty)[\exp(-k''_{obs}t) - \exp(-k''_{obs}t)](k'_{obs} - k''_{obs})^{-1} \quad (1)$$

Results

The use of the basic nucleophile, CN$^-$ in aqueous solution, requires some precautions to avoid hydrolysis, $CN^- + H_2O \longrightarrow HCN + OH^-$, which becomes important in dilute solution. In order to ensure that [CN$^-$] was equal to the stoichiometric amount of KCN added, the reaction mixture was made at least 0.0010 mol dm^{-3} in OH$^-$ but this led to other disadvantages since any reaction by way of the solvolytic path gave rise to hydroxo species, the co-ordinated water being deprotonated faster than it could be replaced by CN$^-$.[24] Addition of KCN to aged solutions of *cis*-$[Pt(NH_3)_2Cl_2]$ and to prepared solutions of *trans*-$[Pt(NH_3)_2(OH)_2]$ led to changes ascribed to the displacement of ammonia followed by very slow spectral changes which only after a very long time led to spectra that resembled that of the tetracyano anion. The displacement of hydroxide by cyanide is therefore very slow. Disturbances by the solvolytic processes were minimal at the higher cyanide concentrations.

The Reactions with Cyanide.—(*i*) *trans*-$[Pt(NH_3)_2(CN)_2]$. The complex *trans*-$[Pt(NH_3)_2(CN)_2]$ is slightly soluble in water and the solution is stable for a number of days and obeys Beer's law. When an aqueous solution (5 × 10^{-4} mol dm^{-3}) is treated with a basic aqueous solution of potassium cyanide at 25 °C the spectrum measured over the wavelength range 220–300 nm changes from that of the substrate to that of an authentic sample of $[Pt(CN)_4]^{2-}$ in a single-stage process with a well defined isosbestic point at 239 nm. When the concentration of CN$^-$ is large enough compared to that of the complex the absorbance change follows a first-order rate law. The rate constants, k_{obs}, collected in Table 1, depend upon [CN$^-$], obeying the usual rate equation, $k_{obs} = k_1 + k_2[CN^-]$. The contribution from the k_1 pathway [$k_1 = (3 \pm 2) \times 10^{-6}$ s^{-1}] is negligible; $k_2 = (4.52 \pm 0.01) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. All derived rate constants are collected in Table 2. The rate constants are also independent of ionic strength. All of these observations indicate that the reaction being followed is the displacement of the first ammonia [equation (2)], the displacement of the second ammonia being fast in comparison.

$$trans\text{-}[Pt(NH_3)_2(CN)_2] + CN^- \longrightarrow [Pt(NH_3)(CN)_3]^- + NH_3 \quad (2)$$

(*ii*) *trans*-$[Pt(NH_3)_2Cl_2]$. The substitution proceeds in two well defined stages; in the presence of sufficient cyanide to avoid interference from the solvolytic stage there is a rapid change to form an intermediate with a spectrum corresponding closely to that of an authentic sample of the *trans*-$[Pt(NH_3)_2(CN)_2]$ complex, Fig. 1. This change is slow enough to be followed kinetically only at the lowest KCN concentrations used, and the rate constants, which are first order in [CN$^-$], give a second-order rate constant of 27 dm^3 mol^{-1} s^{-1}. The rate was independent of ionic strength.

The spectral changes associated with the second stage were very similar to those seen in the reaction of the authentic *trans*-dicyano complex but the isosbestic points were not quite as sharp and the spectrum at the end of this stage was slightly different from that of the tetracyanoplatinate(II) anion. In a third, much slower, stage this difference disappeared. The extent of this disturbance decreased as [CN$^-$] was increased, thereby confirming the hypothesis that there was a diversion of some of the material to relatively inert hydroxo species. The fact that the reactions of the *trans*-$[Pt(NH_3)_2(CN)_2]$ complex were not affected in this way indicated that the disturbance took place in the reactions of the dichloro or chlorocyano species.

The first-order rate constants for the second stage are also collected in Table 1. They vary with [CN$^-$] in the usual first-order fashion, k_{obs}/s^{-1} = (6 ± 8) × 10^{-6} + (4.32 ± 0.05) × 10^{-2}[CN$^-$], and are unaffected by changing the ionic strength. The combined plot of k_{obs} *versus* [CN$^-$] for the reactions of the dicyano and dichloro complexes is shown in Fig. 2, where it will be seen that the [CN$^-$] dependences of the two sets of data are identical within experimental error. The corresponding data for the *cis* isomers are plotted in Fig. 3.

Table 1 Pseudo-first-order rate constants for the reaction with cyanide of various platinum(II) substrates in water at 25 °C

Substrate	I^a/mol dm^{-3}	10^3[OH$^-$]/mol dm^{-3}	10^3[CN$^-$]/mol dm^{-3}	10^3k_{obs}/s^{-1}
trans-$[Pt(NH_3)_2(CN)_2]$	0.401	1.0	0.977	0.0482 ± 0.0005
	0.401	1.0	1.95	0.0942 ± 0.0005
	0.401	1.0	3.91	0.191 ± 0.0003
	0.401	1.0	19.5	0.880 ± 0.005
	0.401	1.0	39.1	1.78 ± 0.01
	0.101	1.0	19.5	0.86 ± 0.013
	0.801	1.0	19.5	0.89 ± 0.007
trans-$[Pt(NH_3)_2Cl_2]^b$	0.500	1.0	0.937	27 ± 0.5
	0.100	1.0	0.937	26.5 ± 0.5
	0.100	1.0	0.28	7.6 ± 0.05
trans-$[Pt(NH_3)_2Cl_2]^c$	0.475	1.0	0.937	0.053 ± 0.001
	0.475	1.0	4.69	0.22 ± 0.008
	0.475	1.0	9.37	0.350 ± 0.08
	0.475	1.0	18.7	0.71 ± 0.05
	0.475	1.0	28.1	1.07 ± 0.06
	0.0146	1.0	4.69	0.210 ± 0.02
	0.0240	1.0	4.69	0.191 ± 0.08
	0.0475	1.0	4.69	0.201 ± 0.05
	0.052	1.0	4.69	0.206 ± 0.05
	0.0994	1.0	4.69	0.205 ± 0.02
cis-$[Pt(NH_3)_2(CN)_2]$	0.475	1.00	25	0.978 ± 0.005
	0.475	1.00	50	1.80 ± 0.10
	0.475	1.00	100	4.35 ± 0.05
cis-$[Pt(NH_3)_2Cl_2]^b$	0.475	1.00	4.69	2.73 ± 0.08
	0.475	1.00	4.69	5.4 ± 0.05
	0.104	1.00	9.37	5.3 ± 0.8
cis-$[Pt(NH_3)_2Cl_2]^c$	0.475	1.00	4.40	0.217 ± 0.008
	0.475	1.00	9.37	0.343 ± 0.005
	0.475	1.00	18.7	0.817 ± 0.005
	0.475	1.00	28.1	1.12 ± 0.05
	0.475	1.00	37.5	1.58 ± 0.02
	0.475	1.00	42.0	1.68 ± 0.008
	0.130	1.00	37.5	1.58 ± 0.05
	0.937	1.00	37.5	1.58 ± 0.06
	0.500	100	41.0	1.35 ± 0.10
	0.500	100	82.0	1.85 ± 0.10
	0.500	100	20.5	1.10 ± 0.8
	0.105	100	4.76	0.227 ± 0.003
	0.200	100	95.2	3.92 ± 0.01
$K[Pt(NH_3)Cl_3]$	0.385	1.00	4.69	6.3 ± 0.9
	0.385	1.00	6.60	7.4 ± 1.0
	0.385	1.00	9.38	10.2 ± 0.5
	0.385	1.00	14.1	12.0 ± 0.8
	0.385	1.00	18.8	19 ± 0.8
	0.385	1.00	28.1	24 ± 0.6
	0.104	1.00	9.37	7.2 ± 0.5
	0.282	1.00	9.37	8.1 ± 0.9
	0.611	1.00	9.37	11.5 ± 0.8
	0.130	1.00	37.5	26.8 ± 0.9
$[Pt(NH_3)_4]Cl_2$	0.475	1.00	41	0.0417 ± 0.008
	0.475	1.00	82	0.0913 ± 0.007
	0.475	1.00	93.7	0.0993 ± 0.001
	0.475	1.00	123	0.142 ± 0.005
	0.475	100	123	0.144 ± 0.008
	0.095	1.00	93.7	0.187 ± 0.005

[a] Ionic strength maintained with $NaClO_4$. [b] The first stage. [c] The second stage.

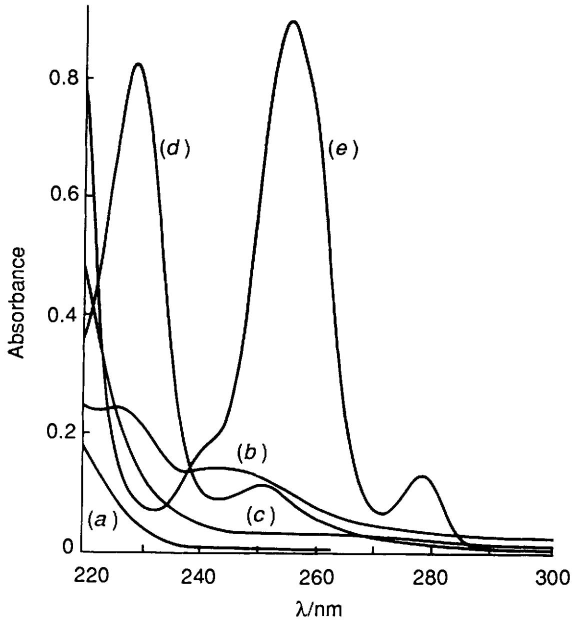


Fig. 1 The UV spectra of fresh aqueous solutions (9×10^{-5} mol dm^{-3}) of (*a*) *cis*-$[Pt(NH_3)_2Cl_2]$, (*b*) *cis*-$[Pt(NH_3)_2(CN)_2]$, (*c*) *trans*-$[Pt(NH_3)_2Cl_2]$, (*d*) *trans*-$[Pt(NH_3)_2(CN)_2]$ and (*e*) $[Pt(CN)_4]^{2-}$

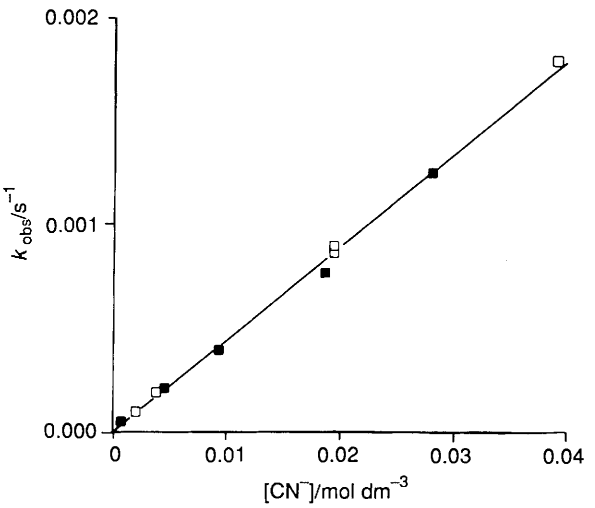


Fig. 2 The dependence of k_{obs} on $[CN^-]$ for the reaction with CN^- of *trans*-$[Pt(NH_3)_2(CN)_2]$ (□) and *trans*-$[Pt(NH_3)_2Cl_2]$ (slow stage) (■)

(*iii*) *cis*-$[Pt(NH_3)_2(CN)_2]$. The complex *cis*-$[Pt(NH_3)_2(CN)_2]$ is sufficiently soluble in water for a kinetic investigation and freshly prepared aqueous solutions obey Beer's law but basic solutions are unstable and their UV spectra change with time. The kinetic studies were therefore carried out with freshly prepared solutions. When a basic solution of KCN is added the spectrum of the reaction mixture changes to one that is very similar to that of an authentic sample of $[Pt(CN)_4]^{2-}$, but not identical; a well maintained isosbestic point is observed at 238 nm and the change in absorbance follows a first-order rate law. The first-order rate constants, which are independent of ionic strength, are also collected in Table 1. They follow the usual two-term relationship, $k_{obs} = k_1 + k_2[CN^-]$, with $k_1 = (2.1 \pm 0.1) \times 10^{-5}$ s^{-1} and $k_2 = (4.01 \pm 0.05) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}.

These results are consistent with a two-stage process in which the displacement of the first ammonia is rate determining [equations (3) and (4)]. At the end of these reactions the spectrum slowly drifts to that of the tetracyanoplatinate(II) ion.

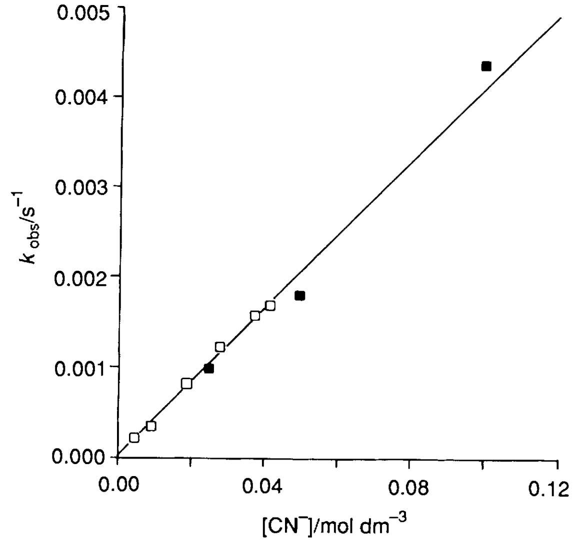


Fig. 3 The dependence of k_{obs} on $[CN^-]$ for the reaction with CN^- of *cis*-$[Pt(NH_3)_2(CN)_2]$ (□) and *cis*-$[Pt(NH_3)_2Cl_2]$ (slow stage) (■)

$$cis\text{-}[Pt(NH_3)_2(CN)_2] + CN^- \longrightarrow [Pt(NH_3)(CN)_3]^- + NH_3 \quad (3)$$

$$[Pt(NH_3)(CN)_3]^- + CN^- \longrightarrow [Pt(CN)_4]^{2-} + NH_3 \quad (4)$$

When a basic solution of *cis*-$[Pt(NH_3)_2(CN)_2]$ is allowed to age there is a small change in its absorption spectrum. This is not large enough to allow a proper kinetic analysis but the half-life is in the region of 5–10 h. When KCN is added to the aged solution the conversion into the $[Pt(CN)_4]^{2-}$ ion takes place in two stages. The spectrum of the intermediate (which has yet to be isolated and characterised) does not differ greatly from that of the tetracyanoplatinate(II) anion so that the data obtained from the analysis of the spectral change in terms of two consecutive first-order reactions lack precision. Both rate constants have a linear dependence on $[CN^-]$ with second-order rate constants of $(3.0 \pm 0.5) \times 10^{-2}$ and $(1.0 \pm 0.5) \times 10^{-4}$ dm^3 mol^{-1} s^{-1} respectively. The first of these rate constants increases with increasing ionic strength indicating that the reacting complex is anionic. A plausible explanation is that the process of ageing leads to the replacement of one ammonia by hydroxide and the two stages of reaction on addition of cyanide are the displacement of ammonia and then hydroxide [equations (5) and (6)].

$$cis\text{-}[Pt(NH_3)(CN)_2(OH)]^- + CN^- \longrightarrow [Pt(CN)_3(OH)]^{2-} + NH_3 \quad (5)$$

$$[Pt(CN)_3(OH)]^{2-} + CN^- \longrightarrow [Pt(CN)_4]^{2-} + OH^- \quad (6)$$

(*iv*) *cis*-$[Pt(NH_3)_2Cl_2]$. Basic solutions of *cis*-$[Pt(NH_3)_2Cl_2]$ are less stable than those of the *trans* isomer and it was necessary to work with freshly prepared solutions in order to achieve reproducible results. This solvolysis, which has been studied extensively,[25–27] is reversible but, in the presence of an excess of hydroxide, *cis*-$[Pt(NH_3)_2(OH)_2]$ is formed. The kinetics of this reaction was studied and it was confirmed that the first-order rate constant increases only slightly with $[OH^-]$ over the range studied. Values for $10^5 k_{obs}/s^{-1}$ for the hydroxide concentrations in parentheses are 1.42 ± 0.02 (0.000 99), 1.45 ± 0.02 (0.0099) and 1.63 ± 0.03 (0.091) at 25.0 °C. Addition of cyanide, in the presence of hydroxide, to a fresh solution of the *cis*-dichloro complex leads to a rapid change of spectrum that is slower and less marked than the first change observed with the *trans* isomer. The new spectrum resembles that of an authentic sample of *cis*-

$[Pt(NH_3)_2(CN)_2]$, Fig. 1. The rate constants for this process were determined from the change in absorbance at 237.5 nm, which is an isosbestic point for the second reaction, and are reported in Table 1. The spectrum then changed slowly to one resembling that of $[Pt(CN)_4]^{2-}$. At the highest cyanide concentrations used the spectral changes for this stage were very similar to those observed in the reaction of the *cis*-$[Pt(NH_3)_2(CN)_2]$ complex, but at lower concentrations of cyanide there was a significant increase in absorbance between 230 and 245 nm in the course of the reaction. This led to a shift of the shoulder at 239 nm in the spectrum at the end of the main reaction to shorter wavelengths and was most pronounced at the lowest $[CN^-]$ where the shoulder changed to a shallow peak. The rate constants for the second stage were obtained by fitting the absorbance *versus* time data at the wavelength of the product peak (254 nm) using a simple first-order rate law as described in the Experimental section. Only those spectra that passed through the isosbestic point were used but the data covered at least four half-lives and the residuals were randomly scattered. The rate constants are collected in Table 1. They are independent of ionic strength and follow the rate equation $k_{obs} = (2 \pm 5) \times 10^{-5} + (4.04 \pm 0.14) \times 10^{-2}[CN^-]$ s^{-1}. The final, and slowest, stage is characterised by a further small increase in the height of the main peak of the spectrum and the difference between the final absorbance and the optimum value for A_∞ for the major change is most significant when the concentration of CN^- is low and is a measure of the importance of the solvolytic disturbance. In the worst case it is only about 10% of the total change.

(*v*) $[Pt(NH_3)Cl_3]^-$. On adding KCN solution to a freshly prepared basic aqueous solution of $K[Pt(NH_3)Cl_3]$ there is an immediate change in the UV spectrum followed by a slower change to that of the $[Pt(CN)_4]^{2-}$ ion as final product. Although the first few spectra pass through a common point at 237.5 nm, the crossing point moves to longer wavelengths as the reaction proceeds. The absorbance *versus* time data can be fitted by a two-exponential process but a statistical analysis of the data does not allow us to say with certainty whether we are indeed looking at two consecutive first-order processes or whether there are two parallel first-order processes. The rate constants for the faster step, which is assigned to the loss of ammonia from the $[Pt(NH_3)(CN)_3]^-$, are collected in Table 1. The set measured at a constant ionic strength ($I = 0.385$ mol dm^{-3}) follow the typical dependence on $[CN]^-$ with $k_1 = 1.8 \times 10^{-3}$ s^{-1} and $k_2 = 0.783 \pm 0.02$ dm^3 mol^{-1} s^{-1}. The observed first-order rate constants increase with increasing ionic strength indicating that the reactant is anionic. The data were extrapolated to zero ionic strength by means of the relationship (7) and a plot of $(k_{obs} - k_1)^0$ against $[CN^-]$ was linear with $k_2{}^0 = 0.348$ dm^3 mol^{-1} s^{-1}.

$$(k_{obs} - k_1)^0 = (k_{obs} - k_1)10^{-1.02I^{\frac{1}{2}}/(1+I^{\frac{1}{2}})} \qquad (7)$$

(*vi*) $[Pt(NH_3)_4]^{2+}$. When alkaline KCN is added to a solution of $[Pt(NH_3)_4]Cl_2$ in water the spectrum changes slowly to that of an authentic sample of $[Pt(CN)_4]^{2-}$. The spectra do not cross and so the isosbestic point test cannot be applied, but the variation of absorbance with time follows a first-order rate law and k_{obs} is independent of the wavelength at which the measurement was made. The rate constants, collected in Table 1, follow the usual rate equation, $k_{obs} = k_1 + k_2[CN^-]$, with $k_1 = (-1 \pm 1.5) \times 10^{-5}$ s^{-1} and $k_2 = (1.24 \pm 0.01) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} for the data collected at $I = 0.475$ mol dm^{-3}. The value of k_{obs} decreases with increasing ionic strength.

(*vii*) $[PtCl_4]^{2-}$. Preliminary studies indicate that the spectrum of the product, even after long reaction times, was not that of pure $[Pt(CN)_4]^{2-}$. There was a peak at 254 nm but the absorbance was too low. It is probable that the solvolytic pathway, leading to the formation of inert hydroxo species, played an important part even at the higher cyanide concentrations. A proper study was reserved until a more suitable solvent could be found.

Discussion

The results of the study of the displacement of ammonia from *trans*-$[Pt(NH_3)_2(CN)_2]$ were clear cut. The reaction took place in a single rate-determining stage; the kinetics was cleanly first order in the presence of a sufficient excess of $[CN^-]$ and followed the usual two-term rate law. The contribution of the solvolytic pathway was negligible at all but the lowest cyanide concentrations and slow subsequent changes, due to the conversion of hydroxo species into $[Pt(CN)_4]^{2-}$, were not observed. These observations were expected and could be accounted for in terms of the fact that the *trans*-labilising effect of CN^- is very much larger than that of NH_3, thus making the rate constant for the displacement of the second ammonia much faster than that for displacement of the first.

The reactions of *trans*-$[Pt(NH_3)_2Cl_2]$ were also readily explained. In the presence of sufficient amounts of CN^-, the spectral changes were identical to those observed in the reaction of the *trans*-dicyano species and the first spectrum measured after the reagents were mixed was identical to that of this complex. In both systems the rate constants are not affected by changing the ionic strength, further confirming that the rate-determining step involved an uncharged complex. Studies with very dilute KCN allowed the first stage of the reaction to be examined but the stopped-flow technique is required for more reliable data to be obtained. A second-order rate constant of 27 dm^3 mol^{-1} s^{-1} can be compared to the value of 5 dm^3 mol^{-1} s^{-1} for the displacement of chloride from *trans*-$[Pt(py)_2Cl_2]$ (py = pyridine) in methanol at 30 °C calculated from the published $n_{Pt}{}^0$ value.

The reaction of *cis*-$[Pt(NH_3)_2(CN)_2]$ with cyanide yielded the $[Pt(CN)_4]^{2-}$ ion in one kinetic stage but was complicated slightly by interference from the parallel reaction with OH^-. The data analysis was able to avoid this interference. The spectral changes associated with the reaction between *cis*-$[Pt(NH_3)_2Cl_2]$ and fairly high concentrations of CN^- were very similar to those observed in the reaction of the dicyano species and the rate constants were identical. It is concluded that both chlorides are displaced from the complex before the ammonia and that the displacement of the first ammonia is rate determining in the subsequent slower stage. At low cyanide concentration it was possible to assign a rate constant to the formation of *cis*-$[Pt(NH_3)_2(CN)_2]$. Under these conditions the interference from the solvolytic side reaction prevented any detailed examination of the homogeneity of the displacement of Cl^- and it is not possible to say whether the two chlorides are replaced at similar rates, or whether one rate constant is very much different from the other. We have assumed that the first displacement is rate limiting but this assumption will have no effect on the subsequent discussion. Data for *cis*-$[Pt(NH_3)_2Cl_2]$ are not available but it can be estimated from the published nucleophilic discrimination factor and intrinsic reactivity that the rate constant for the reaction of CN^- with $[Pt(en)Cl_2]$ (en = ethane-1,2-diamine) is 0.2 dm^3 mol^{-1} s^{-1} in methanol at 30 °C, which is reasonably consistent with the value assigned to the analogous reaction of the *cis*-diammine species in water at 25 °C, 0.58 dm^3 mol^{-1} s^{-1}.

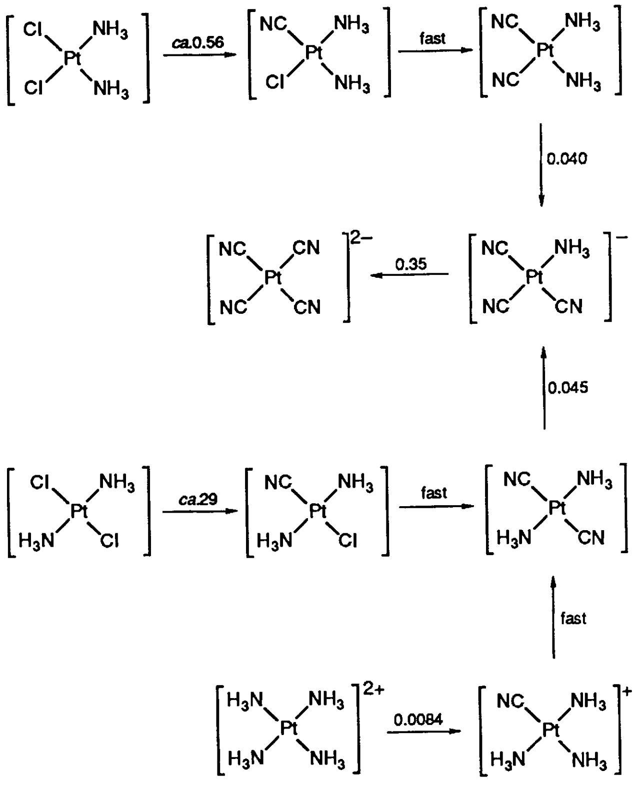
Scheme 1 summarises those processes involving the displacement of chloride or ammonia by cyanide that have been studied in this work but omits the paths that generate or consume hydroxo species. In general, the disturbances created by these side reactions can be taken into account when determining the other rate constants and their contribution is insignificant at higher $[CN^-]$. The derived second-order rate constants shown have been extrapolated to zero ionic strength when the substrate is charged. A number of features stand out.

Much of the behaviour of *trans*-$[Pt(NH_3)_2Cl_2]$ and *trans*-

Table 2 Derived rate constants for the displacement of ammonia from some platinum(II) ammine complexes[a]

Complex used	Reacting substrate	$10^5k_1/\text{s}^{-1}$	$10^2k_2{}^0/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$
trans-$[Pt(NH_3)_2(CN)_2]$	*trans*-$[Pt(NH_3)_2(CN)_2]$	0.3 ± 0.2	4.52 ± 0.01
trans-$[Pt(NH_3)_2Cl_2]$	*trans*-$[Pt(NH_3)_2Cl_2]$	–50[b]	2900[b]
	trans-$[Pt(NH_3)_2(CN)_2]$	0.6 ± 0.8	4.32 ± 0.05
cis-$[Pt(NH_3)_2(CN)_2]$	*cis*-$[Pt(NH_3)_2(CN)_2]$	2.1 ± 0.1	4.01 ± 0.05
cis-$[Pt(NH_3)_2Cl_2]$	*cis*-$[Pt(NH_3)_2Cl_2]$	10[b]	56[b]
	cis-$[Pt(NH_3)_2(CN)_2]$	2 ± 5	4.04 ± 0.14
$K[Pt(NH_3)Cl_3]$	$[Pt(NH_3)(CN)_3]^-$	180 ± 43	34.8 ± 1.0
$[Pt(NH_3)_4]Cl_2$	$[Pt(NH_3)_4]^{2+}$	–1.0 ± 0.5	0.842 ± 0.05

[a] In water at 25.0 °C; $[OH^-] = 0.0010$ mol dm^{-3}, $I = 0$ (data extrapolated where necessary). [b] Rough estimate, insufficient data to establish standard errors.



Scheme 1 A summary of the second-order rate constants (dm^3 mol^{-1} s^{-1}) at 25.0 °C for the entry of CN$^-$ into the complexes indicated. The rate constants for charged substrates are extrapolated to zero ionic strength using the standard expression, $\log k^0 = \log k - [1.02zI^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})]$ where z is the charge on the substrate

$[Pt(NH_3)_2(CN)_2]$ is consistent with the expected behaviour patterns of substitution in square-planar d^8 metal complexes, *e.g.* cyanide is a strong nucleophile and a strong *trans*-effect ligand, chloride is a much better leaving group than ammonia, and *cis*-labilising effects are negligible in comparison to the corresponding *trans* effects. However, compared to the tetraamine complex and the *cis* isomer, the reactivity of *trans*-$[Pt(NH_3)_2(CN)_2]$ is greater than might be predicted. The *cis* complex behaves in a most unexpected manner. The consecutive rate constants for the displacement of the ammonia *trans* to CN ought to be similar, differing only by the required statistical factor and any consequence of the change in the charge of the substrate. In view of the very large difference in the *trans* effects of CN$^-$ and NH$_3$, the similarity of the rate constants for the displacement of ammonia from *cis*- and *trans*-$[Pt(NH_3)_2(CN)_2]$ was puzzling and much effort was devoted to making certain that the identification of the reactions being studied was correct. The evidence that supports the assignments is as follows.

(*a*) The fact that the initial spectra for the reactions of these two isomers with CN$^-$ were very different and corresponded closely to those of the solutions before the cyanide was added rules out any possibility of a rapid isomerisation of these species in solution in the presence of CN$^-$.

(*b*) This observation also rules out the possibility that the displacement of the first ammonia was fast and the rate-determining step was the displacement of the ammonia from $[Pt(NH_3)(CN)_3]^-$, which is, indeed, a common intermediate.

(*c*) The rate constants for the reactions of the *cis* and *trans* isomers are insensitive to changes in the ionic strength indicating that the substrate in the rate-determining step is uncharged.

(*d*) The slowest reaction in the conversion of $[Pt(NH_3)Cl_3]^-$ into $[Pt(CN)_4]^{2-}$ {assumed to be the displacement of ammonia from $[Pt(NH_3)(CN)_3]^-$} has a rate constant that is ten times greater than that of the neutral complexes and responds to changes in ionic strength expected for the reactions of two uninegative ions.

(*e*) It will be shown elsewhere that the rate constants for the reactions of the *cis* and *trans* isomers of complexes of the type $[Pt(am)_2(CN)_2]$ (am = NH$_3$, NH$_2$Me, piperidine, morpholine, and a number of heterocyclic nitrogen bases) with cyanide in methanol can differ considerably from one another.[28]

There are two alternative ways of accounting for these observations. The first is to postulate a very strong *cis*-labilising effect for cyanide that is of a similar magnitude to its well known *trans* effect. The latter is accompanied by a moderately large *trans*- influence (NMR coupling constants indicate that the *trans* influence of cyanide is similar to that of PPh$_3$[29]) and, in principle, co-ordinated CN might function as a π acceptor and add to its *trans* effect by stabilising the five-co-ordinate transition states. There is no indication in Appleton and Bennett's paper,[29] nor elsewhere in the literature, of a noticeable ground-state *cis* influence attributable to cyanide and one must search for an explanation in terms of transition-state stabilisation. The fact remains that, while there is no evidence for significant formation of five-co-ordinate $[Pt(CN)_5]^{3-}$, in the presence of an excess of cyanide, the analogous nickel(II) complex is well known. Two *cis* cyanides, on taking up axial positions in the trigonal bipyramid, can participate in two π orbitals involving the linear N–C–Pt–C–N grouping of atoms. While this might lead to a weakening of the Pt–C bonds as a result of competition for back donation from the metal, it should serve to draw charge away from the metal and so facilitate the bonding with the incoming group.

The second possible explanation is that the strong *trans* influence of cyanide leads to a more open transition state and a greatly reduced nucleophilic discrimination. Thus, for weak nucleophiles, the *trans* effect would be expected to dominate the reactivity. The much greater solvolytic lability of *cis*-$[Pt(NH_3)_2(CN)_2]$ compared to that of its *trans* isomer is compatible with this view. With strong nucleophiles, however, the much higher nucleophilic discrimination of the *trans* isomer where ammonia is exerting a weak *trans* effect may be large enough fortuitously just to overcome the disadvantage of its low intrinsic reactivity. The effect of this can be seen in a comparison of the rate constants for the displacement of Cl^- from *trans*-$[Pt(PEt_3)_2(R)Cl]$ when R = Et (high σ *trans* effect) and Cl (low *trans* effect) in methanol. For a weak nucleophile, *e.g.* solvolysis by methanol, the ethyl complex is some five orders of magnitude more labile than the chloro analogue. However, in the reaction with the strongly nucleophilic thiourea the second-order rate constant for the chloro complex is some three times greater than that of the ethyl species.[30,31]

Thus, in discussing reactivity from the point of view of stabilisation of the transition state or from the point of view of its openness or compactness, it is also important to take into account the contributions made by the entering group and the leaving group and, until there is more information about the dependence of this postulated *cis* effect upon the nature of the entering and leaving group, it would be unwise to speculate any further as to its cause. We are examining the way in which these reactivity patterns are affected by the nature of the leaving group and the entering nucleophile with the intention of choosing between the two hypotheses.

Acknowledgements

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