458. *The Relative Tendencies of Simple Monoamines to form Co-ordination Compounds: The Stability Constants of Some Amine–Platinous Complexes.**

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The equilibrium constants (K_5 and K_6 respectively in Table 1) have been determined for the reactions:

$$C_2H_4PtCl_3^- + am \rightleftharpoons \textit{trans}\text{-}C_2H_4{,}amPtCl_2 + Cl^-$$

and $\textit{trans}\text{-}C_2H_4{,}H_2OPtCl_2 + am \rightleftharpoons \textit{trans}\text{-}C_2H_4{,}amPtCl_2 + H_2O$ where am = an amine. In this way the relatively weak affinity of simple tertiary alkylamines for platinum(II) is quantitatively demonstrated. Possible causes of this weakness are discussed. Two platinous complexes containing simple tertiary alkylamines as ligands have been isolated, *viz.*, *trans*-$C_2H_4{,}NMe_3PtCl_2$ and its 1-methylpiperidine analogue.

Simple tertiary amines, other than heterocyclic amines of the pyridine type, do not usually give co-ordination complexes with salts of the transition metals. On the other hand, the tertiary amino-group will co-ordinate to metals, albeit somewhat weakly, when it is part of a chelate ligand containing a strongly co-ordinating group.[1] Even those metals which are well known for the variety and high stabilities of their complexes, *e.g.*, Co(III), Ru, Os, Rh, Ir, Pd, and Pt, form very few complexes with simple tertiary alkylamines.

The opportunity to obtain some quantitative measure of the relative tendencies of one of these metals to co-ordinate with ammonia and the simple alkylamines was presented by the discovery that the ethylenetrichloroplatinite ion $C_2H_4PtCl_3^-$ behaves as a labile complex so far as the chlorine atom in the *trans*-position to the ethylene molecule is concerned. Leden and Chatt[2] have already used this lability to determine the relative tendencies of platinum(II) to form complexes with the halide ions and thiocyanate ion, and we now record similar determinations of the affinity of ammonia and amines for platinum(II). The methylamines were especially chosen for study because steric effects would be smallest in the series methylamine, dimethylamine, and trimethylamine.

In an aqueous solution of Zeise's salt, $KC_2H_4PtCl_3$, the equilibria (1) and (2) are established immediately.

$$C_2H_4PtCl_3^- + H_2O \rightleftharpoons \textit{trans}\text{-}C_2H_4{,}H_2OPtCl_2 + Cl^- \quad . \; . \; . \quad (1)$$

$$\textit{trans}\text{-}C_2H_4{,}H_2OPtCl_2 \rightleftharpoons \textit{trans}\text{-}C_2H_4PtCl_2{,}OH^- + H^+ \quad . \; . \; . \quad (2)$$

On the addition of an amine salt (amHX) containing an anion (X) of negligible complexing power (such as perchlorate), two further independent equilibria are rapidly established:

$$C_2H_4PtCl_3^- + amH^+ \rightleftharpoons \textit{trans}\text{-}C_2H_4{,}amPtCl_2 + Cl^- + H^+ \quad . \; . \quad (3)$$

$$amH^+ \rightleftharpoons am + H^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

All the species in equations (1)—(4) are in equilibrium with one another, but the constants of the above equilibria are sufficient to define their concentrations. We shall denote these constants by K_1, K_2, K_3, and K_4 respectively. K_1 is small ($3{\cdot}0 \pm 0{\cdot}5 \times 10^{-3}$ at ionic strength 0·2 at 25°).[2] K_2 is of the order[2] of 10^{-5} and K_4 is $<10^{-9}$; in solutions of pH <3 the formation of hydroxy-complex by reaction (2) is scarcely significant, and that of free amine by reaction (4) is sufficiently suppressed to become negligible. Equilibrium (3) is by far the most important in the solution.

The equilibrium constants were determined by measuring the hydrogen-ion concentrations in solutions containing known quantities of Zeise's salt and amine perchlorate.

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* Throughout this paper the square brackets normally used to enclose Werner complexes have been omitted to avoid confusion with square brackets used as a symbol for concentration.

[1] Mann and Stewart, *J.*, 1955, **1269**, and previous references quoted therein.

[2] Leden and Chatt, *J.*, 1955, **2936**.

Allowance was made for the presence of the aqua- and hydroxy-complexes when this was necessary. K_4 was measured independently by using solutions of amine and perchloric acid (Table 1). All measurements were made at an ionic strength of about 0·2 and 23°, and the constants are concentration constants, valid only under those conditions. Amine perchlorate and perchloric acid were used to provide the ionic medium and maintain the ionic strength.

The equilibria of greatest interest are those concerning the direct replacement of a chloride ion or a water molecule by a molecule of monoamine :

$$C_2H_4PtCl_3^- + am \rightleftharpoons \textit{trans}\text{-}C_2H_4,amPtCl_2 + Cl^- \quad . \quad . \quad . \quad (5)$$

$$\textit{trans}\text{-}C_2H_4,H_2OPtCl_2 + am \rightleftharpoons \textit{trans}\text{-}C_2H_4,amPtCl_2 + H_2O \quad . \quad . \quad (6)$$

The former is of interest because most of the common methods available for the preparation of platinous complexes involve the replacement of chloride ion by some other ligand. The latter refers to the formation of the amine complex from the aqua-complex and so is comparable with the stability constants which are available in the literature [3] and refer to the stabilities of the amine complexes of other metals. The constants of the above two equilibria, K_5 and K_6, were therefore evaluated and are listed in Table 1. Their exponents, which are proportional to the free energies of formation of the amine complexes by reactions (5) and (6), are also listed for comparison with existing data of this type.

TABLE 1. *The formation constants of the amine complexes* trans-C_2H_4,amPtCl$_2$ *according to equations* (5) *and* (6), *and the acid dissociation constants* (K_4) *of the ions* amH$^+$, *all at ionic strength* 0·2 *and* 23°.

am	$10^{-4}K_5$	log K_5	$10^{-6}K_6$	log K_6	pK_4
Ammonia	20 ± 3	5·3	67	7·8	9·25 ± 0·03
Methylamine	130 ± 10	6·1	430	8·6	10·74 ± 0·05
Dimethylamine	34 ± 3	5·5	110	8·0	10·86 ± 0·02
Trimethylamine	~0·1	~3·0	~0·3	~5·5	9·89 ± 0·05
Piperidine	50 ± 10	5·7	170	8·2	11·07 ± 0·04
1-Methylpiperidine	2·0 ± 0·5	4·3	7	6·8	10·02 ± 0·05

Certain difficulties, described in the Experimental section, were experienced in the measurements involving the tertiary amines, but there is no doubt about the order of their constants given in Table 1. Attempts to obtain constants for the corresponding equilibria involving aniline and pyridine failed owing to the low solubilities in water of *trans*-C_2H_4,Ph·NH$_2$PtCl$_2$ and *trans*-C_2H_4,pyPtCl$_2$ respectively.

Since the amines are the fourth ligands to enter the platinous complex it might be argued that K_6 should be compared with the fourth stability constants in other metal salt–amine systems. However, the statistical factor will be different because in the platinous system only one and not four amine molecules are held in equilibrium with the solution. It might equally well be argued that K_6 should be compared with first stability constants since it is the first and only amine molecule held by the platinous salt in equilibrium with the solution. However one makes the comparison, the constants are amongst the highest complex formation constants of monodentate amines which have been measured.

The only data sufficiently extensive for comparison are provided by J. Bjerrum's studies [4] of metal ammine formation. It is at once apparent that the constant, $K_6 = 6{\cdot}7 \times 10^7$, is very much higher than the fourth stability constants which have yet been observed in other metal ammine systems. The nearest is in the cobalt(III)–ammonia system and it is estimated to be 7·8 × 10^5 at 30° and ionic strength 2. All those of the bivalent metal ions in the first transition series are less than 150. The more correct comparison is very probably with the first stability constants. Even then K_6 is large, being exceeded only by that in the mercury(II)–ammonia system where the first constant is ~5·6 × 10^8. The first constant in the cobalt(III)–ammonia system is estimated at

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[3] *E.g.*, J. Bjerrum, *Chem. Reviews*, **1950**, **46**, **381**.

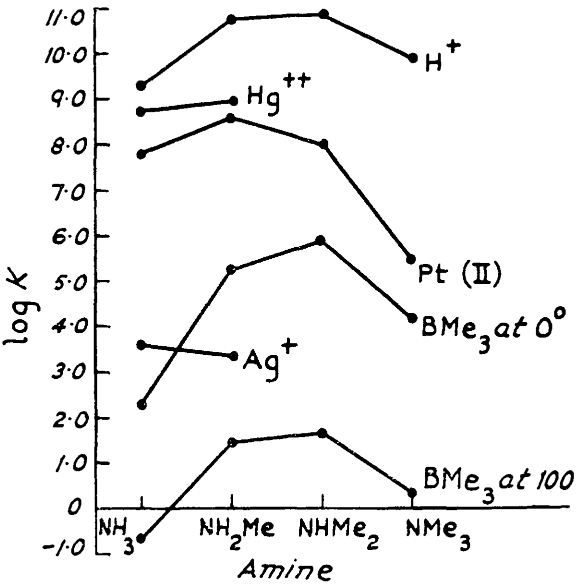
[4] *Idem*, " Metal Ammine Formation in Aqueous Solution," Haas and Son, Copenhagen, **1941**.

2×10^7, but even the most stable of the remaining metal ammine systems which have yet been examined (*e.g.*, Cu^{++} and Ag^+ with ammonia) have first constants $<10^5$.

The low affinities of the trialkylamines for platinum(II) as compared with ammonia are obvious from the constants in Table 1. Unfortunately, the first stability constants of only a few similar systems are available for comparison with these; those few are plotted in the Figure.

Without examining more transition metal–monoamine systems and obtaining heats and entropies of the formation reactions, it is not possible to find out why the tertiary alkylamines co-ordinate to the transition metals so very much more weakly than the less basic ammonia, but the following points are now apparent.

In ammonia and amines the electronic effects of replacing a hydrogen atom by a methyl group increase the electron-donor tendency of the nitrogen atom. Thus, if complex stability depended only on that donor tendency, the stability of the complexes should depend on the amine present in the complex and increase in the order of the amines, $NH_3 < NMeH_2 < NMe_2H < NMe_3$. This order of complex stability has not yet been observed but would probably be found in complex formation with a proton (*i.e.*, " onium " ion formation) in suitable organic solvents.[5] In all systems so far examined, trimethylamine (and other trialkylamines) form weaker complexes than would be expected if the basic strength of ammonia is assumed to be the norm and only electronic effects are taken into consideration. This deviation has been variously attributed to steric effects,[6] solvation effects,[7] a consequence of the electroneutrality principle,[8] and, in the case of the transition metals, to interaction of the NH groups of the amine with *d*-orbitals of the metal atom.[9] Undoubtedly steric repulsion between donor and acceptor molecules (H. C. Brown's F strain) is predominant where bulky acceptor molecules are concerned; *e.g.*, in the gaseous phase with tri-*tert.*-butylborine as acceptor the stabilities of the complexes decrease in the order $NH_3 > NMeH_2 > NMe_2H > NMe_3$.[10] In aqueous solution even the proton complexes (" onium " ions) do not increase uniformly in stability



The relative affinities of ammonia and methylamines for acceptor ions and molecules.

The quantities plotted are :

H^+ : pK_4 at 23° and ionic strength 0·2.

Hg^{++} : $\log ([Hgam^{++}][Hg^{++}]^{-1}[am]^{-1})$,
 (i) at 22° and ionic strength 2·0 for NH_3,
 (ii) at 25° and ionic strength 0·5 for NH_2Me, from ref. (3).

Pt : $\log K_6$ at 23° and ionic strength 0·2.

Ag^+ : $\log ([Agam^+][Ag^+]^{-1}[am]^{-1})$ at 25° and ionic strength 0·5, from ref. (3).

BMe_3 : $\log K_p$ at 0° and 100°, from H. C. Brown.[10]

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[5] Cf. the butylamines, Bell and Bayles, *J.*, 1952, 1578.

[6] H. C. Brown, Bartholomay, Jr., and Taylor, *J. Amer. Chem. Soc.*, 1944, **66**, 435.

[7] (*a*) Trotman-Dickenson, *J.*, 1949, 1293; (*b*) Pearson and Williams, *J. Amer. Chem. Soc.*, 1954, **76**, 258; see also (*c*) Moore and Winmill, *J.*, 1912, **101**, 1635, and (*d*) Frank and Evans, *J. Chem Phys.*, 1945, **13**, 507.

[8] Pauling, *J.*, 1948, 1461; see also Chatt and Wilkins, *J.*, 1952, 4303.

[9] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.

[10] H. C. Brown, *J. Amer. Chem. Soc.*, 1945, **67**, 378.

as hydrogen atoms are replaced by methyl groups; obviously some second factor increasing with increasing methyl substitution counters the electronic effects of methyl substitution (see Figure). Four suggestions as to the nature of this second factor are current. H. C. Brown [6] suggests that it is the steric effect of the greater crowding of the methyl groups in the amine complexes and aminium ions as compared with their less compact arrangement in the free amine (B strain). This effect will increase with increasing methyl substitution. If it accounts for the apparent weakness of tertiary amines relative to primary and secondary amines, there can be no acceptor ion or molecule capable of yielding a complete series of methylamine complexes which increase in stability with increasing *N*-methyl substitution of the amine. According to this explanation ammonia complexes are to be regarded as the most normal, and trimethylamine complexes as weakened by the steric effect.

Trotman-Dickenson [7a] and Pearson and Williams [7b] suggest that the ammonium and aminium ions, and amine complexes in aqueous solution are stabilised by hydration. Strong hydration occurs by virtue of their positive charges and their *N*-hydrogen atoms which form hydrogen bonds to the solvent. Hence the hydration and so the stabilisation of the " onium " ions and complexes decrease with increasing methyl substitution of the amine.

Pauling [8] has applied his principle of electroneutrality to afford an explanation. In complex formation a positive charge develops on the electronegative nitrogen atom. This charge can be dissipated to some extent by distributing it amongst the more electropositive *N*-hydrogen atoms, and so complex formation will be assisted by increasing the number of *N*-hydrogen atoms. The last two explanations are related, because in aqueous solution the formation of hydrogen bonds to the solvent by the *N*-hydrogen atoms will assist still further the dissipation of the positive charge. Chatt, Duncanson, and Venanzi [9] have examined the infrared spectra of a large number of platinous complexes containing primary and secondary amines, and found some evidence of a direct interaction between the NH groups and the *d* or *dp*-hybrid orbitals of the metal atom. They suggested that the complexes containing *N*-hydrogen atoms are stabilised by that interaction, which they represented as a type of hyperconjugation or internal hydrogen bond.

The last three explanations imply that in complex formation trimethylamine is to be regarded as the most normal, and that the complexes of the less highly methylated methylamines are stabilised relative to trimethylamine complexes by virtue of their *N*-hydrogen atoms.

The system which we have examined (eqn. 6) shows a greater weakening of the trimethylamine complexes relative to the other methylamine complexes than is found in any other completely investigated system shown in the Figure. This weakening of the trimethylamine platinous complex relative to the less methylated methylamine complexes cannot be attributed to greater B strain (see above) because this must be roughly constant for all systems. Also, since we are concerned *only* with uncharged species (eqn. 6) which should be less hydrated than ionic species, it cannot be attributed to increased solvation effects of the type suggested by Trotman-Dickenson and by Pearson and Williams. Neither is there any obvious reason why electroneutrality of the nitrogen atoms should be any more difficult to attain in the platinous complex than in the other systems shown in the Figure. It seems that an additional factor must be responsible for the weakness of trimethylamine platinous complexes, and presumably the same factor would account for the almost complete absence of tertiary monoamine complexes of all the later transition metals of each series.

There appear to be two possibilities, (*a*) that the weakness is caused by steric repulsion between the NMe_3 group and the remainder of the *trans*-C_2H_4,NMe_3PtCl_2 molecule (F strain), or (*b*) that the Pt–NH_3 bond is strengthened by interaction of the NH groups with *d*-orbitals of the metal atom.[9] In consideration of (*a*), atomic models show that steric repulsion between the acceptor and donor part of *trans*-C_2H_4,NMe_3PtCl_2 should be about the same as in BMe_3,NMe_3, if we ignore the effects of hydration of the platinous complex. Since it is an uncharged complex it is unlikely to be strongly hydrated. (*a*) is a possible but not very probable cause of the relative weakness of trimethylamine platinous complexes. It would operate only in aqueous solution, whereas the trimethylamine complexes, which we have prepared, are more unstable than the corresponding methylamine complexes, even in the solid state, and in non-aqueous solution. The explanation (*b*) would apply only to complex formation by metals near the end of each transition series. It would account for the fact, known from preparative work, that these metals form the most stable ammines, yet very weak trimethylamine complexes. The existence of an interaction between the *d*-orbitals and NH bonds was first suggested on the basis of spectroscopic evidence. We do not know whether this interaction is sufficiently strong to account for the enhanced stabilities of the platinous complexes of the less methylated methylamines, relative to the trimethylamine complex, but it is a possibility which would explain better than any other hypothesis the few data at present available.

The heterocyclic tertiary aromatic amines, *e.g.*, pyridine, which form stable complexes with the transition metals but have no *N*-hydrogen atoms, may owe the stability of their complexes to the interaction of the *d*-orbitals of the metal with the π-electronic system of the amine.[11]

When *positively charged* complexes of the metals near the ends of each transition series are considered, such an effect as (*b*) would operate together with solvation effects as described by Trotman-Dickenson and by Pearson and Williams. An even greater decrease in stability with increasing replacement of *N*-hydrogen atoms by methyl groups should therefore occur in such complexes. The few data available indicate that it does; *e.g.*, the ammines of silver, cadmium, and mercury have about the same stability as their corresponding monomethylamine complexes (see Fig. and ref. 12).

All the factors discussed above doubtless affect the stabilities of amine complexes in aqueous solution, but many more data are required before their relative importance can be reasonably assessed. Nevertheless the effects of hydration are probably important so far as charged complexes are concerned. The platinous system which we have studied (eqn. 6) is interesting because it concerns only uncharged species in aqueous solution, yet the deviation from the " electronic " order of amine complex stability, *viz.*, $NH_3 < NMeH_2 < NMe_2H < NMe_3$, is greater than in the proton system, $NH_4^+ < NMeH_3^+ < NMe_2H_2^+ > NMe_3H^+$, where the deviation is attributed to solvation enhanced by the positive charge carried by the ions. It seems certain that some factor other than hydration opposes complex formation in the ammines and amine complexes of the transition metals such as platinum, when the *N*-hydrogen atoms are replaced by methyl groups. The nature of the factor is less certain, but the interaction of the *d*-electron pairs in the transition metal with the *N*-hydrogen atoms of the amine is a probable explanation. This would enhance the stabilities of the ammines and less methylated methylamine complexes relative to those of trimethylamine. Similar considerations must apply to other alkylamine systems, but these contain larger alkyl groups, and steric repulsion (F strain) between acceptor and donor molecules or ions must eventually become a predominant factor opposing complex formation.[13]

EXPERIMENTAL

(Microanalyses were made by Messrs. W. Brown and A. G. Olney of these laboratories.)

Materials.—The materials common to this work and that of Leden and Chatt were of the same quality and obtained in the way previously described.[2] Ammonium perchlorate was recrystallised from water and dried at 120°. The amine perchlorates, prepared directly from the amine and acid, are deliquescent and too soluble in water to be recrystallised satisfactorily from it. The three methylamine perchlorates were repeatedly recrystallised from ethanol, and the pyridine perchlorate from ethanol–water (3 : 1). The piperidine and 1-methylpiperidine perchlorates are very soluble even in organic solvents such as ethanol, acetone, and chloroform. They were purified by three precipitations with ether from their acetone and chloroform solutions respectively.

Determination of the Equilibrium Constants.—The constants were calculated from the known constants K_1, K_2, and K_4, and the known initial compositions and measured hydrogen-ion concentrations of solutions containing the ethylenetrichloroplatinite ion and the amine perchlorate.

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[11] Burstall and Nyholm, *J.*, 1952, 3570.

[12] Spike and Parry, *J. Amer. Chem. Soc.*, 1953, **75**, 2726; Fyfe, *J.*, 1955, 1347.

[13] H. C. Brown and Sujishi, *J. Amer. Chem. Soc.*, 1948, **70**, 2878.

The hydrogen ion is liberated in establishing the equilibria (2), (3), and (4) and by the ionisation of the water itself. Since our measurements were carried out at pH <4, the hydrogen ion from the ionisation of water is negligible. The concentration acid dissociation constants (K_4) of the ammonium and methylammonium ions were determined in 0·2M-concentration at 23° by Bjerrum's method.[14] They are listed in Table 1.

Calculation of the constants. The following symbols are used in the tables and mathematical equations for the derivatives of Zeise's salt: $Z = C_2H_4PtCl_3^-$, $Z_{H_2O} =$ *trans*-C_2H_4,H_2OPtCl_2, $Z_{OH} =$ *trans*-$C_2H_4PtCl_2,OH^-$, $Z_{am} =$ *trans*-C_2H_4,am$PtCl_2$. This notation being used, the constants K_1, K_2, and K_4 necessary to calculate K_5 and K_6 are given by:

$$K_1 = [Z_{H_2O}][Cl^-][Z]^{-1} = 3{\cdot}0 \times 10^{-3},\ K_2 = [Z_{OH}][H^+][Z_{H_2O}]^{-1} = 10^{-5},\ K_4 = [H^+][am][amH^+]^{-1}.$$

The required constants are $K_5 = [Z_{am}][Cl^-][Z]^{-1}[am]^{-1}$ and $K_6 = [Z_{am}][Z_{H_2O}]^{-1}[am]^{-1}$. If we represent the initial molar concentrations of any substance, X, by C_X then the quantities and equations necessary to calculate K_5 and K_6 are:

$$[Z_{H_2O}] = K_1[Z][Cl^-]^{-1} \quad \dots \quad (7)$$

$$[Z] = C_Z - [Cl^-] + C_{KCl} \quad \dots \quad (8)$$

$$[Z_{am}] = [H^+] - C_{HClO_4} - [Z_{OH}] - [am] \quad \dots \quad (9)$$

$$[am] = K_4(C_{amHClO_4} - [H^+] + C_{HClO_4} + [Z_{OH}])[H^+]^{-1} \quad \dots \quad (10)$$

$$C_Z = [Z] + [Z_{am}] + [Z_{H_2O}] + [Z_{OH}] \quad \dots \quad (11)$$

In equation (9), [am], and in equation (10), $[Z_{OH}]$ are negligible. Substituting from equations (7), (8), and (9) in equation (11), we find

$$C_Z = C_Z - [Cl^-] + C_{KCl} + [H^+] - C_{HClO_4} + K_1(C_Z - [Cl^-] + C_{KCl})[Cl^-]^{-1}$$

from which

$$2[Cl^-] = C_{KCl} + [H^+] - C_{HClO_4} - K_1 + \{(C_{KCl} + [H^+] - C_{HClO_4} - K_1)^2 + 4K_1(C_{KCl} + C_Z)\}^{\frac{1}{2}} \quad . \quad . \quad (12)$$

Substituting this value of $[Cl^-]$ in equations (7) and (8), we can readily obtain all the quantities necessary to determine K_5; K_6 is obtained from the relation, $K_6 = K_5K_1^{-1}$.

The hydrogen-ion concentration ($[H^+]$) was determined by measuring the e.m.f. (E,mv) of the following cell at 23°:

		$KC_2H_4PtCl_3$	(C_Z)	
+	0·01N-HCl	am$HClO_4$	$(0{\cdot}2\text{M} - C_{HClO_4} - C_{KCl})$	−
Ag,AgCl	0·19M-NH_4ClO_4	$HClO_4$	(C_{HClO_4})	Glass
		KCl	(C_{KCl})	electrode

C_{HClO} and C_{KCl} were zero in most experiments. The reference electrodes Ag,AgCl were prepared as recommended by Brown[15] on 1·4-mm. diameter platinum wire. The cell compartments were joined by a bridge solution of 0·01N-HCl and 0·19M-am$HClO_4$. The potentials (E) were measured in mv, by using a Cambridge pH meter, and were steady except in some of the experiments when trimethylamine and 1-methylpiperidine were investigated. In making a determination a known weight of Zeise's salt, $KC_2H_4PtCl_3$, was placed in the appropriate cell compartment and a known (pipetted) amount (usually 20 c.c.) of 0·2M-amine perchlorate solution was added to it. Solution of the salt and mixing of the solution were effected by passing presaturated nitrogen through the solution for one minute.

The cell was checked without any Zeise's salt or potassium chloride but with various amounts of perchloric acid or with addition of ammonia to show that the e.m.f. obeyed Nernst's law at 23°, $E = E_0 - 58{\cdot}8 \log [H^+]$, over the pH range 2—8·7. The hydrogen-ion concentration in the alkaline range was calculated by using the acid dissociation constant $K_a = 4{\cdot}5 \times 10^{-10}$ for the ammonium ion at 23° and ionic strength 0·2.[16]

[14] Ref. 4, p. 121.

[15] A. S. Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 646.

[16] Everett and Landsman, *Trans. Faraday Soc.*, 1954, **50**, 1221.

The experimentally determined quantities and derived data relating to the various $C_2H_4PtCl_3^-$–amine systems are listed in the Tables 2—7. All concentrations are in molarities (M) at 23°. E_0 is the potential of the cell in mv at 23° for $[H^+] = 1{\cdot}0$ and E is the potential under the conditions of the experiment. All measurements were at 23° and ionic strength 0·2 ($AmHClO_4$). Three glass electrodes were used during these experiments and the different values of E_0 given in the Tables refer to different electrodes. In general, the electrodes were used in pairs to check one another, but since in the experiments recorded in the Tables the two electrodes were always in agreement only one set of data is given.

TABLE 2. *Ammonia.* $E_0 = -93$ mv. $C_{HClO_4} = C_{KCl} = 0$.

10^3C_Z	E	$10^3[H^+]$	$10^8[am]$	$10^3[Cl^-]$	$10^3[Z]$	$10^3[Z_{H_2O}]$	$10^5[Z_{OH}]$	$10^3[Z_{am}]$	$10^{-5}K_5$
0·504	100	0·52	21·62	0·505	0·0	—	—	—	—
2·33	68	1·82	6·11	2·12	0·21	0·30	0·16	1·82	(3·0)
3·14	64	2·13	5·22	2·67	0·47	0·53	0·25	2·13	(2·3)
4·50	59	2·59	4·27	3·48	1·02	0·88	0·34	2·59	2·1
5·91	55	3·03	3·65	4·23	1·68	1·19	0·39	3·03	2·1
7·10	135 *	3·84	2·87	4·54	2·56	1·69	0·44	2·84	1·8
10·67	48	3·99	2·76	6·18	4·49	2·18	0·55	3·98	2·0
19·83	43	4·85	2·26	8·70	11·13	3·84	0·79	4·84	(1·7)
46·23	36	6·38	1·71	13·58	32·65	7·21	1·13	6·37	(1·5)

* In this experiment $E_0 = -7$ mv and $C_{HClO_4} = 1{\cdot}0 \times 10^{-3}$.

TABLE 3. *Methylamine.* $E_0 = -93$ mv. $C_{HClO_4} = 5 \times 10^{-5}$ (acid impurity in the amine perchlorate, not removed by recrystallisation). $C_{KCl} = 0$.

10^3C_Z	E	$10^3[H^+]$	$10^9[am]$	$10^3[Cl^-]$	$10^3[Z]$	$10^3[Z_{H_2O}]$	$10^5[Z_{OH}]$	$10^3[Z_{am}]$	$10^{-6}K_5$
1·36	86	0·90	4·02	1·22	0·14	0·34	0·38	0·85	(1·8)
1·86	81	1·09	3·32	1·58	0·28	0·53	0·49	1·04	(1·8)
3·80	74	1·44	2·50	2·67	1·13	1·27	0·88	1·38	1·3
3·87	73	1·50	2·40	2·72	1·15	1·27	0·85	1·44	1·4
5·69	69	1·75	2·06	3·53	2·16	1·84	1·05	1·69	1·3
8·44	64	2·13	1·69	4·60	3·84	2·50	1·17	2·07	1·5
14·88	61	2·40	1·50	6·37	8·51	4·01	1·67	2·33	1·2

TABLE 4. *Dimethylamine.* $E_0 = -94$ mv. $C_{HClO_4} = C_{KCl} = 0$.

10^3C_Z	E	$10^4(H^+]$	$10^9[am]$	$10^3[Cl^-]$	$10^3[Z]$	$10^3[Z_{H_2O}]$	$10^5[Z_{OH}]$	$10^4[Z_{am}]$	$10^{-5}K_5$
0·711	109	3·52	7·84	0·65	0·06	0·28	0·8	3·44	(4·8)
1·46	100	5·00	5·49	1·19	0·27	0·68	1·4	4·86	(3·9)
2·07	96	5·85	4·69	1·57	0·50	0·96	1·6	5·69	3·8
2·74	94	6·32	4·35	1·91	0·83	1·38	2·2	6·10	3·2
3·44	91	7·11	3·86	2·26	1·18	1·57	2·2	6·89	3·4
4·45	89	7·69	3·57	2·72	1·73	1·91	2·5	7·44	3·3
6·56	85	9·00	3·05	3·51	3·05	2·61	2·9	8·61	3·2
8·86	83	9·73	2·82	4·25	4·61	3·25	3·3	9·40	3·1
12·36	78	11·8	2·33	5·29	7·07	4·01	3·4	11·5	3·7

Trimethylamine.—Considerable difficulty was experienced with this system. In many experiments, immediately after introduction of the glass electrode, the cell potential decreased rapidly, followed by a slow decline. This behaviour was not quite reproducible and did not always occur. Steady potentials were obtained with freshly prepared and recrystallised potassium ethylenetrichloroplatinite. It appeared as if some impurity, which is produced spontaneously in the salt on storage, also caused some catalytic poisoning of the glass electrode. Nevertheless, when the potential of the cell in its variation with time (t) was extrapolated back to $t = 0$ and constants (K_5) were calculated from the extrapolated value, these were all of the order 10^3. Some typical examples are given in Table 5.

TABLE 5. *Trimethylamine.* $C_{HClO_4} = C_{KCl} = 0$.

10^3C_Z	$-E_0$	E	$10^4[H^+]$	$10^8[am]$	$10^3[Cl^-]$	$10^3[Z]$	$10^3[Z_{H_2O}]$	$10^4[Z_{OH}]$	$10^4[Z_{am}]$	$10^{-3}K_5$
5·10	30	184 *	2·30	12·2	2·77	2·33	2·52	1·10	1·20	1·2
6·90	23	192 *	2·21	11·6	3·38	3·52	3·12	1·41	0·80	0·7
10·8	28	182	2·69	9·6	4·56	6·24	4·12	1·53	1·16	0·9
13·2	28	181	2·79	9·25	5·16	8·04	4·68	1·68	1·11	1·2

* Extrapolated value.

trans-*Ethylenetrimethylaminedichloroplatinum.*—$KC_2H_4PtCl_3$ (0·7 g.) was suspended in 3N-hydrochloric acid (1 c.c.) and titrated with 1·0N-trimethylamine to pH = 7. The salt dissolved during the titration and the pale yellow *product* separated gradually. It was filtered off, quickly washed with water and then methanol, and dried at 0·1 mm. pressure (yield, 26%). It decomposed without melting at 105—111° (Found: C, 17·2; H, 3·7; N, 4·0. $C_5H_{13}NCl_2Pt$ requires C, 17·0; H, 3·7; N, 4·0%).

TABLE 6. *Piperidine.* $E_0 = -20$ mv. $C_{HClO_4} = C_{KCl} = 0$.

10^3C_Z	E	$10^4[H^+]$	$10^9[am]$	$10^3[Cl^-]$	$10^3[Z]$	$10^3[Z_{H_2O}]$	$10^5[Z_{OH}]$	$10^4[Z_{am}]$	$10^{-5}K_5$
3·23	163 *	6·08	2·80	2·15	1·08	1·51	2·5	5·83	4·1
4·34	162	8·00	2·13	2·68	1·66	1·86	2·3	7·77	5·9
5·66	163	7·69	2·21	3·16	2·50	2·37	3·1	7·38	4·2
8·33	158	9·35	1·82	4·09	4·24	3·11	3·3	9·02	4·8

* In this experiment $E_0 = -26$ mv.

1-*Methylpiperidine.*—The same difficulty as was experienced in the trimethylamine experiments was also experienced to some extent with 1-methylpiperidine, but in most experiments the cell had a steady potential. The experiment was conducted near the limits of solubility of one of the components in the solution, presumably Z_{am}, and a few minute crystals separated on the bottom of the cell during the course of many experiments. The precipitation was, however, very slow, and during the time of an experiment it was insufficient to affect the potentials.

TABLE 7. 1-*Methylpiperidine.* $E_0 = -23$ mv. $C_{HClO_4} = C_{KCl} = 0$.

10^3C_Z	E	$10^4[H^+]$	$10^8[am]$	$10^3[Cl^-]$	$10^3[Z]$	$10^3[Z_{H_2O}]$	$10^5[Z_{OH}]$	$10^4[Z_{am}]$	$10^{-4}K_5$
1·72	184	2·94	5·53	1·30	0·42	0·97	3·3	2·61	1·5
1·82 *	182	3·18	5·11	2·49	0·67	0·81	2·5	2·93	2·1
2·13	180	3·44	4·73	1·54	0·59	1·15	3·3	3·11	1·7
3·79	170	5·09	3·19	2·36	1·43	1·84	3·6	4·73	2·4
3·98	171	4·90	3·32	2·44	1·54	1·90	3·9	4·51	2·2
7·77	165	6·21	2·62	3·80	3·97	3·13	5·0	5·71	2·1
10·73	162	6·98	2·33	4·65	6·08	3·92	5·6	6·42	2·1

* In this experiment $C_{KCl} = 1·34 \times 10^{-3}$.

trans-*Ethylene*-1-*methylpiperidinedichloroplatinum.*—$KC_2H_4PtCl_3$ (0·6 g.) in 1·0N-hydrochloric acid (4 c.c.) was titrated with 1·2N-1-methylpiperidine. Over the pH range 3—8 the pale yellow *product* gradually separated. It was filtered off, quickly washed with water then methanol, and dried at 0·1 mm. pressure (yield, 30%), decomp. pt. 87—90° (Found: C, 24·4; H, 4·4. $C_8H_{17}NCl_2Pt$ requires C, 24·4; H, 4·4%).

If a more concentrated solution of the salt is titrated 1-*methylpiperidinium ethylenetrichloroplatinite* separates at pH = 1, m. p. 82—82·5° (Found: C, 22·3; H, 4·3. $C_8H_{18}NCl_3Pt$ requires C, 22·4; H, 4·2%). It is followed by precipitation of the above neutral complex at higher pH.

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