Redox Reactions of Platinum-(II) and -(IV) Complexes: Influence of the σ-Donor Ability of Non-labile 2,2'-Bipyridyl and Substituted 1,10-Phenanthroline ligands on the Rates of Reaction

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The reduction of $[PtCl_4(N-N)]$ by $[NBu_4]I$ and the oxidation of $[PtCl_2(N-N]$ by $[AuCl_4]^-$ in the presence of chloride ions have been kinetically investigated in acetonitrile [N–N = 1,10-phenanthroline (phen), 5Me-, $5NO_2$-, $5,6Me_2$-, and $3,4,7,8Me_4$-phen, or 2,2'-bipyridyl(bipy)]. The rate law for the reduction of $[PtCl_4(N-N)]$ has the form: Rate = $k_1[PtCl_4(N-N)] + k_2[PtCl_4(N-N)][I^-]$. The first-order rate term is ascribed to a dissociative Pt–Cl rate-determining bond rupture, followed by a fast redox step. An inner-sphere redox mechanism is thought to be responsible for the second-order rate term. The dissociative path is only slightly affected by changes in N–N, whereas the second-order term is strongly influenced by the σ-donor ability of the uncharged ligands, the relation $\log k_2 = -0.62\ pK_a + 2.05$ being found at 25 °C. The rate law for the oxidation of $[PtCl_2(N-N)]$ by $[AuCl_4]^-$ has the form: Rate = $k_3[PtCl_2(N-N)][AuCl_4^-][Cl^-]$. The rates are not sensitive to changes in N–N, indicating that the energetics of the interactions occurring in the activated complex are on the whole nearly constant throughout the set of ligands employed. A tentative explanation of this behaviour takes into consideration the opposite effects caused by changing N–N on the formation free energy of the precursor inner-sphere intermediate, and on the free energy required to form the transition state for electron transfer from such an intermediate, both effects contributing to the free energy of activation of the redox reaction.

THE kinetics and mechanisms of redox reactions of platinum complexes have been studied for some time and satisfactory information is available on the several possible reaction mechanisms.[1,2] The reason why non-labile ligands bonded to the central metal atom affect the reactivity of platinum complexes towards reduction or oxidation now has a qualitative explanation.[1,2] Thus, for instance, the reactivity of platinum(IV) complexes towards reduction has been suggested to be affected by the extent of σ or π interactions between the ligands and Pt^{IV}.[2] However, the information available in this connection is only qualitative, since it has not yet been possible to distinguish the individual contributions of the σ and π interactions to the reaction rates.

In this paper results are presented on the reductions of platinum(IV) complexes of the type $[PtCl_4(N-N)]$ [N–N = 1,10-phenanthroline (phen), 5Me-, $5NO_2$–, $5,6$-Me_2-, and $3,4,7,8Me_4$-phen, or 2,2'-bipyridyl (bipy)] by $[NBu_4]I$ in acetonitrile, and on the oxidation of the related platinum(II) complexes, $[PtCl_2(N-N)]$, by tetrachloroaurate(III) ions in the presence of $[NEt_4]Cl$, in the same solvent. The choice of the above N–N ligands was made in order to obtain a series of complexes in which the σ-donor ability of the uncharged ligand is known.

EXPERIMENTAL

Materials.—Platinum(II) complexes were prepared following the literature methods.[3] The platinum(IV) complexes were all prepared by the same general method. The parent platinum(II) complex (0.3 g) was dissolved in hot *NN*-dimethylformamide (dmf) (30 cm^3) and treated with hydrogen peroxide and hydrogen chloride. The resulting dark yellow solution was diluted with water (500 cm^3) and left to stand overnight. Yellow microcrystals of $[PtCl_4(N-N)]$ separated. They were filtered off, washed with water, and dried *in vacuo* (Table 1).

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[1] W. R. Mason, *Co-ordination Chem. Rev.*, 1972, **7**, 241.
[2] A. Peloso, *Co-ordination Chem. Rev.*, 1973, **10**, 123.
[3] R. C. Conrad and J. V. Rund, *Inorg. Chem.*, 1972, **11**, 129.

Reagent grade $[NBu_4]I$, $[NBu_4][ClO_4]$, $[NEt_4]Cl$, and $[NEt_4][ClO_4]$ were dried before use. Hydrogen tetrachloroaurate(III) was used as the trihydrate. Acetonitrile was purified by standard methods.[4]

Preparation of the Reaction Mixtures, Stoicheiometry of the Reactions, and Evaluation of the Reaction Rates.—Stock solutions of the compounds employed were prepared by weight. The solutions of the sparingly soluble platinum(II) complexes were filtered to remove undissolved material.

TABLE 1

Analytical data (%); calculated values are given in parentheses

Complex	C	H	N	Cl
$[PtCl_4(phen)]$	28.05	1.60	5.30	27.45
	(27.85)	(1.55)	(5.40)	(27.4)
$[PtCl_4(5Me\text{-}phen)]$	29.75	1.80	5.35	26.0
	(29.4)	(1.90)	(5.25)	(26.7)
$[PtCl_4(5NO_2\text{-}phen)]$	26.05	1.20	7.20	24.75
	(25.65)	(1.25)	(7.45)	(25.25)
$[PtCl_4(5,6Me_2\text{-}phen)]$	30.45	2.35	5.25	25.85
	(30.85)	(2.20)	(5.15)	(26.0)
$[PtCl_4(3,4,7,8Me_4\text{-}phen)]$	33.7	2.75	4.50	24.85
	(33.55)	(2.80)	(4.90)	(24.75)
$[PtCl_4(bipy)]$	24.35	1.80	5.85	28.0
	(24.35)	(1.65)	(5.70)	(28.75)

The concentrations of the platinum complexes and the tetrachloroaurate(III) ions were accurately evaluated spectrophotometrically, by using molar absorption coefficients determined on standard solutions. The reactions were initiated by directly mixing appropriate volumes of thermostatted stock solutions of the reactants in 1-cm silica cells maintained in the thermostatted cell compartment of an Optica CF4R recording spectrophotometer. The reference cell usually contained all the reactants, except the platinum complex, in the same concentration as in the reacting mixture. Only the concentration of Au^{III} was more dilute (*ca.* 10^{-4} mol dm^{-3}) than that of the reacting mixture. The course of the reactions was followed spectrophotometrically by scanning the spectrum of the reacting mixture over the range 400—250 nm at appropriate time intervals. When the reductions of platinum(IV) complexes were fast, the absorbance at 360 nm was recorded against time. The observed rate constants, $k_{obs.}$, were determined from the gradient of plots of log $|D_t - D_\infty|$ against time, where D_t and D_∞ are the absorbances of the reacting mixture at time t and at the end of the reaction.

Reductions of platinum(IV) complexes were carried out at $I = 4.29 \times 10^{-2}$ mol dm^{-3}, obtained by adding the appropriate amount of $[NBu_4][ClO_4]$ to the reacting mixture. The starting concentration of the platinum(IV) complexes was in the range 1×10^{-5}—5×10^{-5} mol dm^{-3}, whereas that of $[NBu_4]I$ was varied in the range 4.29×10^{-3}—4.29×10^{-2} mol dm^{-3} {2.14×10^{-3}—2.14×10^{-2} mol dm^{-3} for the reduction of $[PtCl_4(5NO_2\text{-}phen)]$}. The spectral changes observed in the 400—250 nm region showed that Pt^{IV} reacts with iodide yielding 1 mole of $[I_3]^-$ per mole of Pt^{IV} consumed, with quantitative disappearance of Pt^{IV} at the end of the reaction. Stoicheiometry (1) can be therefore assigned to the reactions between $[PtCl_4(N\text{-}N)]$ and $[NBu_4]I$. It was not determined whether reaction (2) takes place after the redox step. However, separate measurements showed that the spectral changes caused by this substitution reaction are negligible with respect to those occurring during the redox step in the range 300—400 nm. The reactions were followed at 25, 35, and 45 °C. At least six kinetic runs were carried out for each complex at each temperature. Some kinetic runs in the presence of $[NEt_4]Cl$ (1.23×10^{-3}—3.86×10^{-3} mol dm^{-3}) were also performed. The reduction of Pt^{IV} to Pt^{II} was also quantitative in these cases, while the spectra of the reaction mixtures indicate that chloroiodo-species, such as $[I_2Cl]^-$ and $[ICl_2]^-$, are present in the solution together with $[I_3]^-$.

$$[PtCl_4(N\text{-}N)] + 3I^- \longrightarrow [PtCl_2(N\text{-}N)] + [I_3]^- + 2Cl^- \quad (1)$$

$$[PtCl_2(N\text{-}N)] + 2I^- \longrightarrow [PtI_2(N\text{-}N)] + 2Cl^- \quad (2)$$

The oxidations of the platinum(II) complexes were carried out at $I = 0.1$ mol dm^{-3} obtained by adding the appropriate amount of $[NEt_4][ClO_4]$ to the reacting mixtures. The starting concentration of the platinum(II) complexes was within the range 1×10^{-5}—5×10^{-5} mol dm^{-3}; the ranges of concentration explored for the other reactants were as follows: $[NEt_4]Cl$, 2.00×10^{-2}—1.00×10^{-1}; $HAuCl_4$, 3.42×10^{-4}—3.42×10^{-3} mol dm^{-3}. The platinum(II) complexes underwent quantitative oxidation to Pt^{IV} according to stoicheiometry (3), which was determined as in a previous paper.[5] The reactions were examined at 35 and 50 °C. At least four sets of kinetic runs were carried out using different gold(III) concentrations, each set involving at least four runs in which the concentration of $[NEt_4]Cl$ was changed.

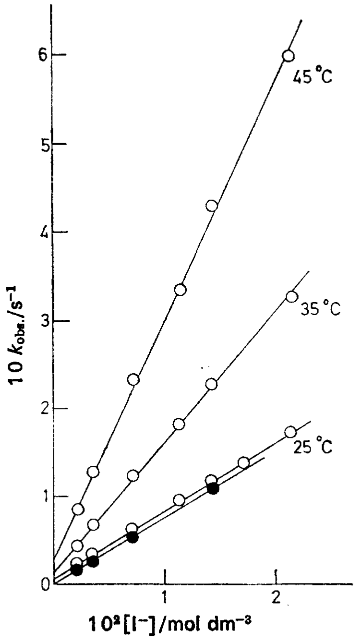

FIGURE 1 Observed rate constants, $k_{obs.}$, for the reduction of $[PtCl_4(5NO_2\text{-}phen)]$ by $[NBu_4]I$ in acetonitrile, as a function of the concentration of iodide ions in the absence (○) or in the presence (●) of free chloride (3.6×10^{-3} mol dm^{-3})

$$[PtCl_2(N\text{-}N)] + [AuCl_4]^- \longrightarrow [PtCl_4(N\text{-}N)] + [AuCl_2]^- \quad (3)$$

RESULTS AND DISCUSSION

Reduction of the Platinum(IV) *Complexes*.—The reactions, carried out in the presence of a large excess of

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[4] A. Weissberger, 'Organic Solvents,' Interscience, New York, 1955.

[5] A. Peloso, *Co-ordination Chem. Rev.*, 1975, **16**, 95.

$[NBu_4]I$, obeyed equation (1), and followed a pseudo-first-order rate law. A two-term rate law (4), accounts for the dependence of $k_{obs.}$ on the concentration of iodide (*e.g.* Figure 1). The values of k_1 and k_2 obtained for each complex are collected in Table 2, together with the

$$-d[PtCl_4(N\text{-}N)]/dt = k_1[PtCl_4(N\text{-}N)] + k_2[PtCl_4(N\text{-}N)][I^-] \quad (4)$$

related activation parameters. The pattern in k_1 is ascribed to a dissociative Pt–Cl rate-determining bond rupture, followed by a fast redox step. An inner-sphere redox mechanism, involving a direct interaction in the activated complex between the reducing agent and a chloride ligand on Pt^{IV}, of the type encountered in the reduction of other platinum(IV) complexes by iodide and other reducing agents,[2] is probably responsible for the second-order reaction path. The overall mechanism for the reduction by iodide of the complexes under discussion is in equations (5a)—(5d).

TABLE 2

Rate constants and activation parameters [a] for the reduction of $[PtCl_4(N\text{-}N)]$ by $[NBu_4]I$ in acetonitrile at $I = 4.29 \times 10^{-2}$ mol dm^{-3}

N-N	θ_c °C	10^4k_1 s^{-1}	$\Delta H_1^‡$ kJ mol^{-1}	$\Delta S_1^‡$ J K^{-1} mol^{-1}	10^2k_2 dm^3 mol^{-1} s^{-1}	$\Delta H_2^‡$ kJ mol^{-1}	$\Delta S_2^‡$ J K^{-1} mol^{-1}
phen	25	1.5			6.64		
	35	2.7			13.5	55	−84
	45	5.2			28.8		
5Me-phen	25	1.5			5.90		
	35	3.1			12.4	52	−92
	45	5.5			23.7		
$5NO_2$-phen	25	5.0			78.0		
	35	12			150	48	−88
	45	26			283		
5,6Me_2-phen	25	3.30 [b]			4.26		
	35	6.00 [b]	40.5	−175	9.08	56	−84
	45	10.0 [b]			18.7		
3,4,7,8Me_4-phen	25	1.23 [b]			1.47		
	35	2.35 [b]	46	−167	3.33	58	−80
	45	4.17 [b]			6.80		
bipy	25	1.7			4.91		
	35	3.6			11.1	54	−88
	45	8.8			20.5		

[a] Standard deviations: $k_1 \pm 12\%$; $k_2 \pm 2\%$; $\Delta H_1^‡ \pm 8$ kJ mol^{-1}; $\Delta S_1^‡ \pm 20$ J K^{-1} mol^{-1}; $\Delta H_2^‡ \pm 2$ kJ mol^{-1}; $\Delta S_2^‡ \pm 5$ J K^{-1} mol^{-1}. [b] ±6%.

$$[PtCl_4(N\text{-}N)] + MeCN \underset{\text{fast}}{\overset{k_1}{\rightleftharpoons}} [PtCl_3(N\text{-}N)(NCMe)]^+ + Cl^- \quad (5a)$$

$$[PtCl_3(N\text{-}N)(NCMe)]^+ + I^- \xrightarrow{\text{fast}} [PtCl_2(N\text{-}N)] + ICl + MeCN \quad (5b)$$

$$[PtCl_4(N\text{-}N)] + I^- \xrightarrow{k_2} [PtCl_2(N\text{-}N)] + ICl + Cl^- \quad (5c)$$

$$ICl + 2I^- \xrightarrow{\text{fast}} \left\{ \begin{array}{c} [I_3]^- + Cl^- \\ \downarrow\uparrow \\ [I_2Cl]^- + I^-, \textit{etc.} \end{array} \right\} \quad (5d)$$

According to this mechanism, the addition of $[NEt_4]Cl$ to the reacting mixture lowers the contribution to the rate due to the dissociative path, whereas no effect is observed on the k_2 rate term (*e.g.* Figure 1). Although a detailed analysis of the kinetic effect of chloride ions was not made, a ratio of $[Cl^-] : [I^-]$ higher than 2 : 1 was sufficient to remove the contribution of the dissociative path to the reduction rates. The rates of such a path appear to be only slightly affected by changes in the uncharged ligands N–N (Figure 2), the specific rate constants, k_1, at 25 °C being always in the range 1.23×10^{-4}—5.0×10^{-4} s^{-1}. Conversely, the second-order reaction path is very sensitive to changes in N–N, a reactivity order $5NO_2$-phen > phen > 5Me-phen > bipy > 5,6Me_2-phen > 3,4,7,8Me_4-phen being observed. Such a trend appears to be governed only by the enthalpies of activation, since the entropies of activation are nearly constant (*ca.* −86 J K^{-1} mol^{-1}) throughout the series

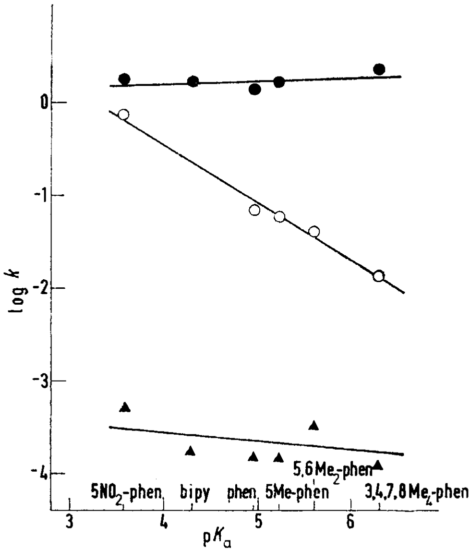

FIGURE 2 Dependence of the specific rate constant on the basicity of N–N: reduction of $[PtCl_4(N\text{-}N)]$ by $[NBu_4]I$ [k_1, (▲); k_2, (○)] at 25 °C; oxidations of $[PtCl_2(N\text{-}N)]$ by $[AuCl_4]^-$ [k_3, (●)] at 35 °C

(Table 2). Apart from the complex with bipy, the above sequence may be rationalized quantitatively in terms of the σ-donor ability of the uncharged ligands N–N, as measured by their basicity.[6] Figure 2 shows that log k_2 is linearly dependent on the pK_a of N–N, according to relation (6), where $a = 0.62 \pm 0.05$ and $b = 2.05 \pm 0.26$.

$$\log k_2 = -a\mathrm{p}K_a + b \qquad (6)$$

Therefore, the σ-donor ability of a ligand appears to be a good parameter with which to quantitatively correlate the relative reactivities of similar platinum(IV) complexes towards reduction. Relation (6) probably results from the effect of the σ interactions between N–N and Pt^{IV} on the standard reduction potential of the platinum(IV) complexes, $E^\ominus$ (Pt^{IV}–Pt^{II}). The free energy of activation for inner-sphere reductions of platinum(IV) complexes, $\Delta G^\ddagger$, is thought to be related to the standard free energy of the redox reaction, $\Delta G^\ominus$, by equation (7).[7]

$$\Delta G^\ddagger = c\Delta G^\ominus + \text{constant} \qquad (7)$$

This implies that the specific rate for the reductions of complexes of the type $[PtCl_4(N{-}N)]$ by iodide will increase on increasing the value of $E^\ominus(Pt^{IV}{-}Pt^{II})$, since $\Delta G^\ominus = -nFE^\ominus(Pt^{IV}{-}Pt^{II})$ + constant. The reduction potential of a complex is generally thought to increase linearly with the electron affinity of the central metal atom,[8,9] which, in turn, is postulated to parallel the decreasing contribution from the ligands to the electron density on the metal.[10] In the complexes $[PtCl_4(N{-}N)]$ under discussion, the σ-donor ability increases with increasing pK_a of N–N. On the basis of this contribution only, the reduction potential is expected to increase linearly with $-$pK_a, thus leading to a linear increase in log k_2 with decreasing pK_a values, as found experimentally. This fact suggests that, apart from the complex with bipy, the σ interactions are dominant in determining the reactivity towards reduction of the platinum(IV) complexes, the effect caused by changes in the π contributions being comparatively negligible. The complex with bipy exhibits a significantly lower reactivity than that expected on the basis of the pK_a of the ligand. In the case of bipy, the Pt–N π bonding may be sufficiently different from that exhibited by phen ligands (the ability of bipy rings to delocalize electrons being lower than that expected for phen) to explain the failure of $[PtCl_4(bipy)]$ to fit equation (6). In the reduction of other complexes containing bipy or substituted phen ligands, the complexes with bipy have been found to react more slowly than would be expected on the basis of correlations between rates and non-kinetic parameters.[11,12]

Oxidation of Platinum(II) *Complexes*.—The oxidation of the platinum(II) complexes, $[PtCl_2(N{-}N)]$, by tetrachloroaurate(III) ions, in the presence of $[NEt_4]Cl$ is governed by stoicheiometry (3) and follows a pseudo-first-order rate law. The observed rate constant, $k_{obs.}$, is linearly dependent on the concentration of either Au^{III} or chloride (Figure 3), according to the third-order rate law (8). It is not clear whether a first-order contribution to the rate is also operating, as previously found for the

$$-\mathrm{d}[PtCl_2(N{-}N)]/\mathrm{d}t = k_3[PtCl_2(N{-}N)][AuCl_4^-][Cl^-] \qquad (8)$$

oxidation of other platinum(II) complexes by the same oxidizing agent.[5] However, the contribution of this path is too small for a reliable evaluation of its specific rate constant, k_s. The order of magnitude of k_s and the values of k_3 obtained are collected in Table 3 together with the related activation parameters.

TABLE 3

Rate constants and activation parameters for the oxidation of $[PtCl_2(N{-}N)]$ by hydrogen tetrachloroaurate in acetonitrile

N–N	θ_c / °C	k_3 / dm^6 mol^{-2} s^{-1}	$\Delta H_3^\ddagger$ / kJ mol^{-1}	$\Delta S_3^\ddagger$ / J K^{-1} mol^{-1}	k_s / s^{-1}
phen	35	1.42	27	−155	*ca.* 4×10^{-6}
	50	2.44			$<1 \times 10^{-5}$
5Me-phen	35	1.67	29	−147	$<5 \times 10^{-6}$
	50	2.95			$<10^{-5}$
5NO$_2$-phen	35	1.83	26	−155	$<10^{-5}$
	50	3.07			$<10^{-5}$
3,4,7,8Me$_4$-phen	35	2.39	28	−142	*ca.* 0
	50	4.20			*ca.* 0

Standard deviations: $k_3 \pm 3\%$; $\Delta H_3^\ddagger \pm 4$ kJ mol^{-1}; $\Delta S_3^\ddagger \pm 10$ J K^{-1} mol^{-1}.

The rate of the third-order reaction path, with which we will only be concerned, appears to be independent of the ligand N–N considered (Figure 2). Both the enthalpies and the entropies of activation (Table 3) are constant along the series. Whatever the reaction mechanism operating,[5] the lack of any dependence of the rates on the uncharged ligands N–N seems to suggest that the energetics of the interactions of Pt^{II} with chloride and $[AuCl_4]^-$ ions in the transition state are on the whole nearly constant throughout the set of ligands employed. An explanation of these results could be that such interactions are very weak. In fact changes in N–N cause changes in the ability of Pt^{II} both to undergo attack by a nucleophile,[3] such as chloride which is to be co-ordinated, and to release electrons. If significant interactions were occurring in the transition state, one would expect some

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[7] A. J. Poë and D. H. Vaughan, *J. Amer. Chem. Soc.*, 1970, **92**, 7537.

[8] A. A. Vlcek, *Progr. Inorg. Chem.*, 1967, **5**, 211.

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[10] S. Ahrland and J. Chatt, *J. Chem. Soc.*, 1957, 1379.

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dependence of the rates on N–N. An alternative explanation, which takes into consideration the possibility of significant interactions in the transition state, can be tentatively proposed. The free energy of activation of these inner-sphere redox reactions includes the free energy of formation of the precursor intermediate, $[PtCl_2(N\text{–}N), AuCl_4^-, Cl^-]$, and the so-called rearrangement free energy, *i.e.* the free energy required to form the transition state for the electron transfer from such a precursor.[13,14] The formation of the precursor intermediate is expected to be favoured by ligands with low pK_a values, since the nucleophilic attack of chloride, either as a free ion or bonded to Au^{III}, on Pt^{II} is favoured when the electron density on the metal is lowered.[3] Thus, the trend of the formation free energy of the precursor intermediate would be expected to be in the order $3,4,7,8Me_4$-phen > 5Me-phen > phen > bipy > $5NO_2$-phen. As far as the rearrangement free energy is concerned, this is thought to increase on increasing the standard free energy of the redox reaction,[15,16] *i.e.* with increasing $E^{\ominus}(Pt^{IV}\text{–}Pt^{II})$, since $\Delta G^{\ominus} = nF[E^{\ominus}(Pt^{IV}\text{–}Pt^{II}) - E^{\ominus}(Au^{III}\text{–}Au^{I})]$. Therefore (see above), the trend in the rearrangement free energy is expected to be in the order $5NO_2$-phen > bipy > phen > 5Me-phen > $3,4,7,8Me_4$-phen. The opposite effects of the ligands N–N on the two energy terms would tend to cancel out, thus giving rise to the observed invariance of the free energy of activation.

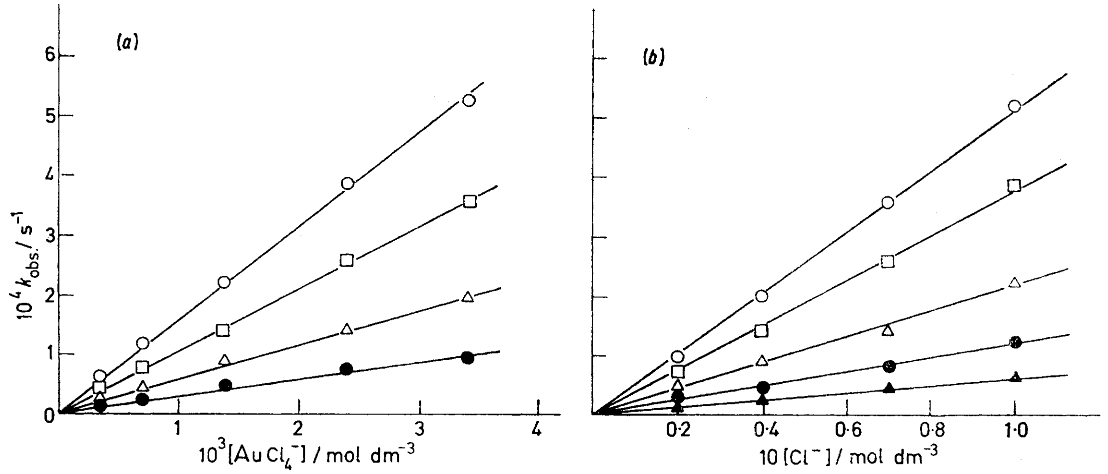

FIGURE 3 Oxidation of $[PtCl_2(phen)]$ by $[AuCl_4]^-$ in acetonitrile at 35 °C: (*a*) dependence of $k_{obs.}$ on $[AuCl_4^-]$ in $[NEt_4]Cl$ [1.0×10^{-1} (○), 7.0×10^{-2} (□), 4.0×10^{-2} (△), and 2.0×10^{-2} mol dm^{-3} (●)]; (*b*) dependence of $k_{obs.}$ on [Cl$^-$] in $[AuCl_4^-]$ [3.42×10^{-3} (○), 2.40×10^{-3} (□), 1.37×10^{-3} (△), 6.25×10^{-4} (●), and 3.42×10^{-4} mol dm^{-3} (▲)]

[5/1888 *Received*, 30*th September*, 1975]

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