Kinetics of Oxidation of Dichlorobis(substituted pyridine)platinum(II) and of Reduction of Tetrachlorobis(substituted pyridine)platinum(IV) Complexes

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The kinetics of oxidation of *cis*-$[PtCl_2L_2]$ by $[AuCl_4]^-$ in the presence of $[NEt_4]Cl$ and of the reduction of *cis*-$[PtCl_4L_2]$ by $[NEt_4]I$ have been investigated in acetonitrile [L = pyridine (py), 3Me-, 2Me-, $2,4Me_2$-, 3Cl-, 4Cl-, 3CN-, or 4CN-py]. The rate law for the oxidation of *cis*-$[PtCl_2L_2]$ has the form: Rate = $k_3[PtCl_2L_2][AuCl_4^-][Cl^-]$. The k_3 rate term is not affected by changes in the co-ordinated pyridine and has a value *ca.* 100 times higher than that previously found for related phenanthrolineplatinum(II) complexes. The rate law for the reduction of *cis*-$[PtCl_4L_2]$ has the form: Rate = $k_2[PtCl_4L_2][I^-]$. The k_2 rate term is strongly influenced by the basicity of L according to an identical relation to that previously found for the reduction of related phenanthrolineplatinum(IV) derivatives. The kinetic results are discussed in terms of σ and π interactions between the central metal atom and the heterocyclic ligands.

IN a previous paper[1] I reported the results of a kinetic investigation on the reduction of platinum(IV) complexes of the type $[PtCl_4(N-N)]$ [N–N = 1,10-phenanthroline (phen), substituted 1,10-phenanthrolines, and 2,2′-bipyridyl (bipy)] by $[NBu_4]I$ and the oxidation of the related platinum(II) complexes, $[PtCl_2(N-N)]$, by tetrachloroaurate(III) anion in acetonitrile. It was found that the rates of reduction of the platinum(IV) complexes are strongly affected by the basicity of N–N, whereas this factor has no influence on the rate of oxidation of the related platinum(II) complexes. The different effect displayed by the ligands used on the rates of oxidation of platinum(II) and the reduction of platinum(IV) complexes were so peculiar as to deserve further investigation.

In this paper I report kinetic studies of the oxidation of *cis*-$[PtCl_2L_2]$ [L = pyridine (py), 3Me-py, 3Cl-py, 4Cl-py, 3CN-py, 4CN-py, 2Me-py, or $2,4Me_2$-py] by $[AuCl_4]^-$ in the presence of $[NEt_4]Cl$ and of the reduction of *cis*-$[PtCl_4L_2]$ (L = py, 3Me-py, 3Cl-py, 4Cl-py, 3CN-py, or 4CN-py) by $[NEt_4]I$ in acetonitrile. The aim of the work was to compare the reactivities of the above complexes with those of the related substituted phen derivatives which differ from the former mainly in the different spatial arrangement[2-4] and π-accepting ability[5,6] of the *cis*-co-ordinated heterocyclic rings.

EXPERIMENTAL

Materials.—Platinum(II) complexes, *cis*-$[PtCl_2L_2]$, were prepared by standard methods.[7] The salt $K_2[PtCl_4]$ (1 mmol) was treated with the ligand (2.2 mmol) in water (5 cm^3). The required pale yellow complexes slowly precipitated out from the mixture under stirring at room temperature. They were filtered off, washed several times with water, and dried *in vacuo*. The complex *trans*-$[PtCl_2(py)_2]$ was prepared by the literature method.[8] Platinum(IV) complexes were prepared by the method previously described for the related phenanthrolineplatinum(IV) complexes.[1] The parent platinum(II) complex (*ca.* 0.3 g) was dissolved in hot dimethylformamide (*ca.* 10 cm^3) and treated with hydrogen chloride and hydrogen peroxide. The resulting dark yellow solution was diluted with water (*ca.* 100 cm^3) and left to stand overnight. Yellow complexes of formula $[PtCl_4L_2]$ separated (Table 1). They were filtered off, washed with small volumes of water, and dried *in vacuo*. The *cis* configuration was assumed on the basis of the fact that oxidation of platinum(II) complexes $[PtCl_2L_2]$ leads to platinum(IV) derivatives in which the relative positions of the uncharged ligands are preserved.[9]

TABLE 1

Analytical data (%) with calculated values in parentheses

Complex	C	H	N	Cl
cis-$[PtCl_4(3Me\text{-}py)_2]$	27.4 (27.55)	2.65 (2.70)	5.35 (5.35)	26.85 (27.1)
cis-$[PtCl_4(3Cl\text{-}py)_2]$	20.6 (21.3)	1.40 (1.45)	4.80 (4.95)	36.8 (37.7)
cis-$[PtCl_4(4Cl\text{-}py)_2]$	21.0 (21.3)	1.35 (1.45)	4.80 (4.95)	
cis-$[PtCl_4(3CN\text{-}py)_2]$	25.9 (26.45)	1.45 (1.50)	10.6 (10.25)	25.75 (26.0)
cis-$[PtCl_4(4CN\text{-}py)_2]$	26.3 (26.45)	1.55 (1.50)	10.6 (10.25)	26.3 (26.0)

Reagent grade $[NEt_4][ClO_4]$, $[NEt_4]Cl$, and $[NEt_4]I$ were dried before use. Hydrogen tetrachloroaurate(III) was used as the trihydrate. Acetonitrile was purified by standard methods.[10]

Preparation of the Reaction Mixtures, Stoicheiometry of the Reactions, and Evaluation of the Reaction Rates.—The preparation of stock solutions and reaction mixtures and the evaluation of the pseudo-first-order rate constants, $k_{obs.}$, were as described previously.[1] The reactions were followed spectrophotometrically by scanning the spectrum of the reacting mixture over the range 270—370 nm at appropriate time intervals. Fast reactions were followed by recording the absorbance against time at a selected wavelength [360 nm for the reduction of platinum(IV) complexes and within the 295—310 nm region for the oxidation of platinum(II) complexes].

The oxidations of the platinum(II) complexes were carried

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out at $I = 0.1$ mol dm^{-3} with [NEt$_4$][ClO$_4$] as supporting electrolyte. The starting concentration of the platinum(II) complexes was 1.0×10^{-5}—1.0×10^{-4} mol dm^{-3}. The concentration of [NEt$_4$]Cl was varied in the range 1.00×10^{-2}—5.50×10^{-2} mol dm^{-3} {down to 5.00×10^{-3} mol dm^{-3} for the oxidation of *cis*-[PtCl$_2$(3Cl-py)$_2$] and *trans*-[PtCl$_2$(py)$_2$]}. The ranges of concentration of HAuCl$_4$ explored for the oxidations were as follows: (*i*) *cis*-[PtCl$_2$(3CN-py)$_2$], 2.73×10^{-4}—2.73×10^{-3}; (*ii*) *cis*-[PtCl$_2$(4CN-py)$_2$], 5.96×10^{-4}—1.73×10^{-3}; (*iii*) *cis*-[PtCl$_2$(2Me-py)$_2$], *cis*-[PtCl$_2$(3Me-py)$_2$], *cis*-[PtCl$_2$(2,4Me$_2$-py)$_2$], and *cis*-[PtCl$_2$(4Cl-py)$_2$], 5.45×10^{-4}—1.64×10^{-3}; (*iv*) *cis*-[PtCl$_2$(py)$_2$], 5.76×10^{-4}—1.78×10^{-3}; (*v*) *cis*-[PtCl$_2$(3Cl-py)$_2$], 5.76×10^{-4}—1.21×10^{-3}, and (*vi*) *trans*-[PtCl$_2$(py)$_2$], 2.88×10^{-4}—8.63×10^{-4} mol dm^{-3}.

The reactions were found to obey stoicheiometry (1). The oxidation product was recovered from an exhausted

$$cis\text{-(or } trans\text{-)[PtCl}_2\text{L}_2] + [\text{AuCl}_4]^- \longrightarrow cis\text{-(or } trans\text{-)[PtCl}_4\text{L}_2] + [\text{AuCl}_2]^- \quad (1)$$

reaction mixture (starting concentration of Pt$^{\text{II}}$, *ca.* 1.0×10^{-3} mol dm^{-3}) by precipitation with water. The crude product, contaminated by some [NEt$_4$][AuCl$_4$], was purified by dissolution in acetonitrile and precipitation with water. The analytical data and u.v. spectrum agreed with those required by [PtCl$_4$L$_2$]. Moreover, the spectral changes observed during the reaction showed that 1 mol of Au$^{\text{III}}$ is consumed per mol of Pt$^{\text{IV}}$ produced. The reactions were examined at 30 and 50 °C. For each complex and at any given temperature 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.

Reductions of platinum(IV) complexes were carried out at $I = 5.14 \times 10^{-2}$ mol dm^{-3} with [NEt$_4$][ClO$_4$] as supporting electrolyte. The starting concentration of the platinum(IV) complexes was 1.0×10^{-5}—5.0×10^{-5} mol dm^{-3}. The ranges of concentration explored for [NEt$_4$]I were 1.71×10^{-3}—5.14×10^{-2} (L = 3Me-py and 4Cl-py), 6.86×10^{-3}—5.14×10^{-2} (L = py), 5.14×10^{-4}—3.43×10^{-2} (L = 3Cl-py), 5.14×10^{-4}—5.14×10^{-3} (L = 4CN-py), and 4.28×10^{-4}—2.57×10^{-3} mol dm^{-3} (L = 3CN-py). The spectral changes observed in the 280—370 nm region showed that Pt$^{\text{IV}}$ reacts with iodide yielding 1 mol of [I$_3$]$^-$ per mol of Pt$^{\text{IV}}$ consumed, according to stoicheiometry (2). The reduction product, *cis*-[PtI$_2$L$_2$], was isolated from

$$cis\text{-[PtCl}_4\text{L}_2] + 5\,\text{I}^- \longrightarrow cis\text{-[PtI}_2\text{L}_2] + [\text{I}_3]^- + 4\,\text{Cl}^- \quad (2)$$

an exhausted reaction mixture (starting concentration of Pt$^{\text{IV}}$, *ca.* 1×10^{-3} mol dm^{-3}) by precipitation with water. The overall reaction (2) is probably the result of the redox step (3) and the subsequent nucleophilic substitution (4) on the primary reduction product, *cis*-[PtCl$_2$L$_2$], as is usually found in the reactions of platinum(IV) complexes

$$cis\text{-[PtCl}_4\text{L}_2] + 3\,\text{I}^- \longrightarrow cis\text{-[PtCl}_2\text{L}_2] + [\text{I}_3]^- + 2\,\text{Cl}^- \quad (3)$$

$$cis\text{-[PtCl}_2\text{L}_2] + 2\,\text{I}^- \longrightarrow cis\text{-[PtI}_2\text{L}_2] + 2\,\text{Cl}^- \quad (4)$$

with iodide.[11] In a separate experiment it was found that spectral changes caused by the occurrence of reaction (4) are negligible with respect to those caused by the formation of [I$_3$]$^-$ in the 350—370 nm region where the evaluation of $\log|A_t - A_\infty|$ was made. The reactions were followed at 25 and 45 °C (20 and 35 °C for L = 3CN-py). At least six kinetic runs were carried out at different concentrations of [NEt$_4$]I for each complex at each temperature.

RESULTS

All the reactions followed a pseudo-first-order rate law. The pseudo-first-order rate constant, $k_{\text{obs.}}$, for the oxidation of platinum(II) complexes was linearly dependent on both the gold(III) and chloride concentrations according to the third-order rate law (5). The pseudo-first-order rate constant for the reduction of the platinum(IV) complexes

$$-\text{d[PtCl}_2\text{L}_2]/\text{d}t = k_3[\text{PtCl}_2\text{L}_2][\text{AuCl}_4^-][\text{Cl}^-] \quad (5)$$

$$-\text{d[PtCl}_4\text{L}_2]/\text{d}t = k_2[\text{PtCl}_4\text{L}_2][\text{I}^-] \quad (6)$$

was linearly dependent on the concentration of [NEt$_4$]I according to the second-order rate law (6). No evidence was obtained for a reduction path independent of the iodide concentration, of the type found to operate in the reduction of [PtCl$_4$(N–N)] complexes.

TABLE 2

Rate constants and activation parameters [a] for the oxidation of *cis*-[PtCl$_2$L$_2$] by HAuCl$_4$ in acetonitrile

L	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}
3Cl-py	30.0	313		
	50.0	540	20	−130
3Me-py	30.0	195		
	50.0	285	13	−160
3CN-py	30.0	580		
	50.0	870	14	−145
4Cl-py	30.0	440		
	50.0	683	15	−145
4CN-py	30.0	352		
	50.0	556	16	−145
py	30.0	222		
	50.0	316	12	−160
py [b]	30.0	255		
	50.0	378	13	−155
2Me-py	30.0	no reaction		
2,4Me$_2$-py	30.0	no reaction		

[a] Standard deviations: $k_3 \pm 4\%$; $\Delta H_3^\ddagger \pm 6$ kJ mol^{-1}; $\Delta S_3^\ddagger \pm 20$ J K^{-1} mol^{-1}. [b] *trans* Complex.

TABLE 3

Rate constants and activation parameters * for the reduction of *cis*-[PtCl$_4$L$_2$] by [NEt$_4$]I in acetonitrile

L	θ_c / °C	k_2 / dm^3 mol^{-1} s^{-1}	$\Delta H_2^\ddagger$ / kJ mol^{-1}	$\Delta S_2^\ddagger$ / J K^{-1} mol^{-1}
py	25.0	5.66×10^{-2}		
	45.0	3.16×10^{-1}	65	−50
3Me-py	25.0	3.83×10^{-2}		
	45.0	2.15×10^{-1}	65	−52
4Cl-py	25.0	4.21×10^{-1}		
	45.0	1.96	58	−57
3Cl-py	25.0	2.38		
	45.0	15.0	70	−3
4CN-py	25.0	9.70		
	45.0	63.8	72	+14
3CN-py	20.0	8.40		
	35.0	23.3	48	−62

* Standard deviations: $k_2 \pm 3\%$; $\Delta H_2^\ddagger \pm 4$ kJ mol^{-1}; $\Delta S_2^\ddagger \pm 12$ J K^{-1} mol^{-1}.

The values of the specific rate constants, k_3 and k_2, obtained in each case are reported in Tables 2 and 3, together with the related activation parameters.

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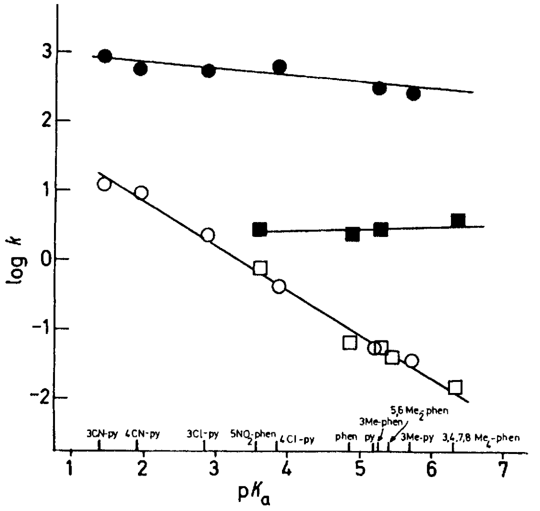
[11] A. Peloso, *Co-ordination Chem. Rev.*, 1973, **10**, 123 and refs. therein.

DISCUSSION

Rate laws (5) and (6) have essentially the same form as those previously found for the oxidation-reduction reactions of analogous platinum complexes of substituted phenanthrolines.[1] The activation entropies {with the exception of those for the reduction of *cis*-[$PtCl_4$(4CN-py)$_2$] and *cis*-[$PtCl_4$(3Cl-py)$_2$]} are also comparable. These facts suggest that complexes with both types of ligands undergo redox reactions with a similar mechanism. In particular, the reduction of platinum(IV) complexes is thought to occur by an inner-sphere mechanism involving an activated complex, $[Cl_3L_2Pt{-}Cl \cdots I]^-$, of the type previously postulated for the reduction of several platinum(IV) complexes by iodide and other reducing agents.[11] The mechanism operating in the oxidation of platinum(II) complexes by $[AuCl_4]^-$ is not yet well understood, although it probably involves an interaction either between $[AuCl_4]^-$ and an unstable five-co-ordinate platinum(II) complex, $[Cl_2L_2Pt{-}Cl]^-$, or between the starting platinum(II) complex and pentachloroaurate(III), $[AuCl_5]^{2-}$.[12]



Dependence of the rate constant on L or N–N for reduction of *cis*-[$PtCl_4L_2$] (○) and [$PtCl_4$(N–N)] (□) at 25 °C and oxidation of *cis*-[$PtCl_2L_2$] (●) and [$PtCl_2$(N–N)] (■) at 50 °C. Data for N–N were taken from ref. 1

Both types of uncharged ligands considered also display strikingly analogous behaviour in affecting the reaction rates (see Figure). For instance, it is found that the rates of oxidation of platinum(II) complexes are generally independent of the nature of the co-ordinated ligand. In particular, no dependence on pK_a is generally observed, provided that platinum(II) complexes of substituted pyridines or substituted phenanthrolines are considered separately. However, there is no doubt that the ligands affect the oxidation rate since although the reactivity does not change on changing the ligands within the same class it strongly increases on going from phenanthrolines to pyridines, the increase (*ca.* 100-fold) being mainly caused by a decrease in the enthalpy of activation (*e.g.* for N–N = phen, $\Delta H_3^\ddagger = 27$ kJ mol^{-1}, $\Delta S_3^\ddagger = -155$ J K^{-1} mol^{-1}: for L = py, $\Delta H_3^\ddagger = 12$ kJ mol^{-1}, $\Delta S_3^\ddagger = -160$ J K^{-1} mol^{-1}). The independence of the oxidation rates of pK_a has been tentatively ascribed in a previous paper as the consequence of the opposite effects caused by changes of pK_a both on the free energy of formation of the intermediate prior to the electron transfer, [$PtCl_2$(N–N), $AuCl_4^-$, Cl^-], and on the rearrangement free energy required to form the transition state from such a precursor.[1] The results obtained with platinum(II) complexes of substituted pyridines do not allow a better explanation of the observed trend. Apart from this question, it appears that the higher reactivity of platinum(II) complexes of substituted pyridines with respect to analogous phen derivatives must arise from some property which is a function of the type of ligand, but which remains essentially constant when ligands of the same type are considered. I think that this property is the different ability of pyridines and phenanthrolines to act as π acceptors. From the results of nucleophilic substitutions and i.r. measurements it has been suggested that the spatial arrangement of the aromatic rings of bipy in [$PtCl_2$(bipy)] is such as to produce an aromatic system with eight π electrons in the five-membered ring formed on co-ordination.[5,6] This behaviour is to be expected also with phenanthrolines as ligands but not with pyridines.[5] As a consequence, phenanthrolines will cause greater withdrawal of electron density from Pt^{II} than pyridines, thus making the related complexes more inert toward oxidation. In this connection the high inertness of platinum(II) complexes of *ortho*-substituted pyridines (see Table 2) is probably attributable to steric effects. In fact, *o*-methyl groups tend to occupy a position over and below the plane of the complex, pointing toward the platinum atom, which is therefore sterically protected from oxidative attack.[13]

Conversely, the rates of reduction of platinum(IV) complexes are strongly affected by the co-ordinated ligand, whatever it is, *i.e.* substituted phenanthrolines or pyridines. Moreover, the reactivity at 25 °C, expressed in terms of log k_2, is linearly related to the pK_a values of the ligands by relation (7), which is fully satisfied by all the platinum(IV) complexes of substituted phenanthroline and pyridines examined (see Figure).

$$\log k_2 = -0.63\ \mathrm{p}K_a + 2.07 \qquad (7)$$

This behaviour indicates that in these cases the rates of reduction of the platinum(IV) complexes are affected only by σ metal–nitrogen interactions, and that π interactions play a much less important part in reduction of this type of platinum(IV) complex than in the oxidation of the related platinum(II) derivatives. Of course, such differences in π interactions are not unexpected in view of the fact that the reaction centre for oxidation [*i.e.* the central atom Pt^{II}] is different from that of reduction (*i.e.* one of the co-ordinated chloride ions). However, it is to be noted that π interactions in

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platinum(IV) complexes are expected to be less important than those operating in platinum(II) derivatives, whereas σ interactions are comparatively more important due to the higher effective nuclear charge on platinum in platinum(IV) derivatives. In fact, the higher electron affinity of Pt^{IV} relative to Pt^{II} would enhance the dative σ N→Pt bond, whereas the Pt→N back donation would be decreased. If π back donation in platinum(IV) complexes is negligible, the electron affinity of Pt^{IV} will be essentially related to the σ-donor ability of the co-ordinated ligands. Since the latter can be determined from the pK_a of the ligands,[14] it is expected that the electron affinity of Pt^{IV} will increase linearly with $-$pK_a, *i.e.* in the same direction as the tendency of Pt^{IV} to undergo reduction.[15,16]

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