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Reduction Reactions of *trans*- PtL_2X_4 Complexes. Influence of the Uncharged Ligands L on the Reduction Reaction Rates

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Kinetic investigations on redox reactions of platinum(IV) complexes of the type trans-[PtL_2X_4] *(where L = pyridine, piperidine, methyl- and ethylamine, dimethyl- and diethylsulphide; X = Cl or Br) with* SCN^-, I^-, $SeCN^-$ *and* $S_2O_3^{2-}$ *in methanol are reported. All of the substrates studied are reduced by these anions to platinum(II) complexes; the reaction rates are first order with respect to both the platinum(IV) complex and the reducing anion. The reduction rates of the complexes* trans-[PtL_2X_4] *increase in the order arsine < phosphine < amine < thioether. This trend is accounted for by the different σ-donor and π-acceptor ability of the uncharged ligands L.*

Introduction

In previous papers[1-4] we have investigated the reduction reactions of platinum(IV) complexes of the type *cis*- and *trans*-[PtL_2X_4] (where L = phosphine or arsine; $X_4 = Cl_4, Cl_2Br_2, Br_4$) with NaSCN, NaI, KSeCN and $Na_2S_2O_3$ in methanolic solutions. It has been found that all of the complexes studied are reduced to platinum(II) complexes in a process involving a bimolecular attack between the substrate and the reducing anion. The rates of the redox reactions of the various substrates with the different reducing anions were found to obey the following linear free energy relationship:

$$\log k_2 = r(X) + r_s \qquad (1)$$

where k_2, is the rate constant for the bimolecular reaction between the substrate and the reducing anion, at 40°C; r(X) is the value of $\log k_2$ for the corresponding reaction of *trans*-[$Pt(P(C_3H_7)_3)_2Cl_4$], selected as standard substrate;[2] r_s is a constant for a given substrate.[2,4] The results obtained from the investigation of various substrates ascertained that the redox reaction proceeds through an inner-sphere electron-transfer mechanism involving a weak bond formation between one of the halogens coordinated, acting as electron mediator, and the reducing anion in the activated complex.[3,4] For the examined isostructural complexes with the same halogens coordinated, it was found that the relative reactivity of the substrates, *i.e.* the values of r_s, depends upon the nature of the uncharged ligand L.[4]

In order to obtain further informations on the role played by the ligand L in determining the rate of reduction of platinum(IV) complexes, it was decided to extend the kinetic investigations to other complexes of the type *trans*-[PtL_2Cl_4], having L = $S(CH_3)_2$, $S(C_2H_5)_2$, NH_2CH_3, $NH_2C_2H_5$, piperidine and pyridine. Moreover, the kinetic investigations were extended to *trans*-[PtL_2Br_4] (L = $S(C_2H_5)_2$, NH_2CH_3, and $NH_2C_2H_5$) in order to see whether a significant change in the nature of L will affect the difference of reactivity between corresponding chloro- and bromo-compounds; this difference was found previously to remain constant when L is changed from arsine to phosphine.[3] NaSCN, NaI, KSeCN and $Na_2S_2O_3$ were employed as reducing salts. All the reactions were carried out in methanolic solutions.

Experimental Section

Materials. The complexes *trans*-[$Pt(NH_2CH_3)_2Br_4$], *trans*-[$Pt(NH_2C_2H_5)_2Br_4$], and *trans*-[$Pt(pip)_2Cl_4$], (pip = piperidine) were prepared by treating chloroformic solutions of the corresponding platinum(II) complexes with an excess of bromine or chlorine, respectively. The solutions were evaporated and the products were recrystallized from methanol. *trans*-[$Pt(NH_2CH_3)_2Br_4$] was isolated as a red powder, which decomposes at 212 °C (Calcd.: C, 4.16; H, 1.75; Br, 55.4; N, 4.86; Found: C, 4.2; H, 1.9; Br, 53.2; N, 5.0).

trans-[$Pt(NH_2C_2H_5)_2Br_4$] was isolated as a red powder, which decomposes at 210°C (Calcd.: C, 8.0; H, 2.33; Br, 52.8; N, 4.63; Found: C, 8.2; H, 2.2; Br, 50.4; N, 4.5).

trans-[$Pt(pip)_2Cl_4$] was isolated as a yellow powder, which melts at 210°C (Calcd.: C, 23.7; H, 4.37; Cl, 27.9; N, 5.52; Found: C, 23.9; H, 4.2; Cl, 26.9; N, 5.3).

The isomeric form was assigned on the basis of the preparation method: the oxidation of platinum(II) complexes of the type [PtL_2X_2] by halogens, X_2, is known to give generally platinum(IV) complexes of the type [PtL_2X_4] in which the ligands L retain the same relative position (*cis* or *trans*) as in the starting com-

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(1) A. Peloso and G. Dolcetti, *J. Chem. Soc.*, (A), 000 (1967).
(2) A. Peloso, G. Dolcetti and R. Ettorre, *Gazz. Chim. Ital.*, *97*, 955 (1967).
(3) A. Peloso, G. Dolcetti and R. Ettorre, *Gazz. Chim. Ital.*, *97*, 1507 (1967).
(4) A. Peloso, R. Ettorre and G. Dolcetti, *Inorg. Chim. Acta*, *1*, 307 (1967).

plex.[5] The other complexes used were prepared following the methods reported in literature.[6] Methanol was distilled over $Mg(OCH_3)_2$. All the other reagents were reagent grade.

Kinetics. Relatively slow reactions were carried out by mixing the appropriate volumes of thermostatted solutions of the reactants directly in 1 cm quartz cells in the thermostat-controlled cell compartment of an Optica CF4R spectrophotometer. At suitable time intervals the spectrum of the reacting mixture was scanned over the range 240-360 mμ. In the case of relatively fast reactions, the absorbance at a selected wavelength in the U.V. region was recorded against time.

Very fast reactions were followed spectrophotometrically by means of a stopped-flow apparatus, which consisted of a Beckman DU spectrophotometer to which was attached a rapid mixing device, thermostatted at the desired temperature. The change in transmittance with time at the appropriate wavelength was displayed on a Tecktronix 564 storage oscilloscope.

Almost all of the reactions (see Table I) were carried out at two temperatures, at least four different concen-

Table I. Rate constants, k_2, and activation parameters for the redox reactions: *trans*-$[PtL_2X_4]^- + Y^{n+} \rightarrow$ Products; in methanol. The concentration of the substrate was in the range 1×10^{-5}-$1\times10^{-4}M$

N	Complex	Reagent	Concn. range of reagent (mole × 1^{-1})	Temperature (°C)	k_2 (l × $mole^{-1}$ × sec^{-1})	ΔH* (kcal × $mole^{-1}$)	ΔS* (e.u.)
(1)	*trans*-$[Pt(S(C_2H_5)_2)_2Cl_4]$	NaSCN	0.20 - 0.034	40	1.26×10^{-2}		
				25	0.34×10^{-2}	15.6	—18
		NaI	4.3×10^{-3} - 7.1×10^{-4}	40	9.25		
				25	3.40	11.8	—17
		KSeCN	1.3×10^{-3} - 3.4×10^{-4}	40	78		
				25	36	9	—21
		$Na_2S_2O_3$	2×10^{-3} - 3.5×10^{-4}	30	11.8×10^2		
				20	6.6×10^2	9.7	—12
				40 [a]	2.2×10^3		
(2)	*trans*-$[Pt(S(CH_3)_2)_2Cl_4]$	NaSCN	0.21 - 0.043	40	1.10×10^{-2}		
				25	0.36×10^{-2}	13.2	—25
		NaI	4.3×10^{-3} - 7×10^{-4}	40	9.5		
				25	3.82	10.5	—21
		$Na_2S_2O_3$	1×10^{-3} - 2.5×10^{-4}	30	3×10^3		
				20	1.6×10^3	10.5	— 8
				40 [a]	5.4×10^3		
(3)	*trans*-$[Pt(pip)_2Cl_4]$	NaI	4.3×10^{-2} - 1.1×10^{-2}	40	29×10^{-2}		
				25	9×10^{-2}	13.8	—17
		$Na_2S_2O_3$	1×10^{-3} - 4×10^{-4}	40	1.6×10^2	—	—
(4)	*trans*-$[Pt(py)_2Cl_4]$	NaI	4.6×10^{-2} - 1.1×10^{-2}	40	1.7×10^{-1}		
				25	0.64×10^{-1}	11.5±1.5	—22±5
		$Na_2S_2O_3$	1×10^{-3} - 4×10^{-4}	40	36		
				25	12.5	12.5	—11
(5)	*trans*-$[Pt(NH_2C_2H_5)_2Cl_4]$	NaI	0.26 - 0.043	50	8.6×10^{-2}		
				35	2.15×10^{-2}	17.6	— 9
				40 [a]	3.6×10^{-2}		
		$Na_2S_2O_3$	1.7×10^{-3} - 2.9×10^{-4}	40	86		
				25	23	15.7	0
(6)	*trans*-$[Pt(NH_2CH_3)_2Cl_4]$	NaI	0.26 - 0.043	50	3.1×10^{-2}		
				35	0.68×10^{-2}	19.4	— 5
				40 [a]	1.1×10^{-2}		
		$Na_2S_2O_3$	2.1×10^{-3} - 5×10^{-4}	50	84		
				35	26	14.8	— 4
				40 [a]	52		
(7)	*trans*-$[Pt(S(C_2H_5)_2)_2Br_4]$	NaSCN	1.7×10^{-3} - 5.7×10^{-4}	40	52		
				25	22	10±2	—20±6
		NaI	1×10^{-3} - 4×10^{-4}	30	2.3×10^4		
				20	1.48×10^4	7.4	—15
				40 [a]	3.5×10^4		
(8)	*trans*-$[Pt(NH_2C_2H_5)_2Br_4]$	NaSCN	1.7×10^{-2} - 4.2×10^{-3}	40	5.2×10^{-1}		
				25	1.22×10^{-1}	17.3	— 5
		NaI	1×10^{-2} - 2.5×10^{-3}	30	2.02×10^2		
				20	1.06×10^2	10.8	—12
				40 [a]	3.7×10^2		
(9)	*trans*-$[Pt(NH_2CH_3)_2Br_4]$	NaSCN	3.5×10^{-2} - 1.4×10^{-2}	40	2.5×10^{-1}		
				25	0.6×10^{-1}	17	— 7
		NaI	1.4×10^{-3} - 4.4×10^{-4}	40	1.72×10^2		
				25	0.6×10^2	12.4	— 9
		$Na_2S_2O_3$	1×10^{-3} - 3×10^{-4}	30	8×10^4		
				20	4.1×10^4	11.3	1
				40 [a]	1.5×10^5		

[a] Extrapolated or interpolated data.

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(5) R. G. Wilkins and M. J. G. Williams, in J. Lewis and R. G. Wilkins, eds., *Modern Coordination Chemistry, Interscience*, N.Y., p. 200 (1960).

(6) Gmelins Handbuch der Anorganische Chemie, *68*, Teil D, Verlag Chemie G.M.B.H. (1957).

trations of the reducing salt being employed for each temperature. The pseudo-first order rate constants were determined from the slope of the plots of log-$|D_\infty - D_t|$ against time, where D_t and D_∞ are the optical densities of the reacting mixture at the time t and after at least five half-lives, respectively.

Results

The reactions were carried out in presence of a sufficient excess of the anionic reagent, Y^{n-}, over the complex, in order to achieve the pseudo first-order conditions. The reproducibility of the rate constants was generally better than 5%.

No attempts were made to keep the ionic strength constant, in view of the zero charge on the complex. The linearity of the plots of the rate constants *vs* salt concentration ascertains that the ionic strength changes do not play an important role on the rates.

All the reactions studied follow the kinetic law given by equation (2):

$$-d[\mathrm{Complex}]/dt = k_2[\mathrm{Complex}][Y^{n-}] \qquad (2)$$

The second order rate constants, k_2, obtained at the different temperatures are listed in Table I together with the activation parameters. The estimated error in ΔH^* is ±1 kcal/mole and in ΔS^* is ±3 e.u., unless otherwise stated.

(a) *Reactions of* trans-[$Pt(S(C_2H_5)_2)_2Cl_4$], trans-[$Pt(S(C_2H_5)_2)_2Br_4$] trans-[$Pt(S(CH_3)_2)_2Cl_4$], trans-[$Pt(NH_2CH_3)_2Br_4$] *and* trans-[$Pt(NH_2C_2H_5)_2Br_4$] *with NaSCN in methanol.* The analysis of the spectral changes of the reacting mixtures showed that the platinum(IV) complexes react with NaSCN in a single stage. The very close agreement between the final spectrum of the reaction between *trans*-[PtL_2X_4] and thiocyanate and the spectrum of a solution of *trans*-[$PtL_2(SCN)_2$] in concentration equal to that of the initial *trans*-[PtL_2X_4] showed that the reaction product is in any case *trans*-[$PtL_2(SCN)_2$]. This product, however, undergoes a successive slower reaction, probably a decomposition or a polymerization reaction, particularly in the case of the thioethers derivatives.

It has not been possible to obtain satisfactory data for the reaction of thiocyanate with the other complexes listed in Table I, due to the fact that the decomposition or polimerization reaction has a rate comparable with that of the redox reaction.

(b) *Reaction of all the substrates with NaI in methanol.* The reactions were studied using the usual spectrophotometric tecnique, except the reactions of complexes *trans*-[$Pt(S(C_2H_5)_2)_2Br_4$] and *trans*-[$Pt(NH_2C_2H_5)_2Br_4$], which were studied by means of the stopped-flow tecnique. The spectral changes of the reacting mixtures showed that I_3^- is formed during the reaction, in a single step, the final spectrum corresponding to that of a solution of I_3^- and *trans*-[PtL_2I_2] in equimolecular amount with respect to the initial platinum(IV) complex. Moreover, in all of the cases the reaction product containing platinum could be identified as *trans*-[PtL_2I_2] from the analysis of the final spectra of reacting mixtures in which I_3^- was eliminated by addition of $Na_2S_2O_3$ in equivalent amount. The reaction product of *trans*-[$Pt(pip)_2Cl_4$] is the same which is formed in the reaction: *trans*-[$Pt(pip)_2Cl_2$] + I^-.[7]

(c) *Reaction of* trans-[$Pt(S(C_2H_5)_2)_2Cl_4$] *with KSeCN in methanol.* In this case two consecutive reactions were observed. By selecting appropriate wavelengths, it was possible to calculate the rate of the first reaction. Although it was not possible to identify the reaction products, previous observations suggest that the first stage of these reactions involves the reduction of the initial platinum(IV) complex.[4]

(d) *Reactions of* trans-[PtL_2Cl_4] ($L = S(CH_3)_2$, $S(C_2H_5)_2$, NH_2CH_3, $NH_2C_2H_5$, *piperidine, pyridine*) *and* trans-[$Pt(NH_2CH_3)_2Br_4$] *with* $Na_2S_2O_3$ *in methanol containing 4,3% of water.* Water (4,3%) was added to dissolve the sodium salt. All of the reactions were followed by means of the stopped-flow technique, except the reactions of the complexes *trans*-[$Pt(NH_2CH_3)_2Cl_4$] and *trans*-[$Pt(py)_2Cl_4$] (py = pyridine), which were followed using the usual technique. The analysis of the final spectra of the reacting mixtures indicated that the reaction product for the tetrabromo-complexes is *trans*-[$PtL_2(S_2O_3)_2$]$^{2-}$. This product is formed during the reaction in single step, *i.e.* without formation of any intermediate in detectable amount. In the case of tetrachloro-complexes, *trans*-[PtL_2Cl_2] is the first reaction product, which then undergoes a slower substitution reaction, the final product being *trans*-[$PtL_2(S_2O_3)_2$]$^{2-}$. Reactions carried out with an excess of *trans*-[PtL_2Cl_4] with respect to the thiosulphate present showed that two thiosulphate ions are consumed for each platinum(II) that is reduced.

Discussion

The analysis of the products and stoicheiometry of the reactions show that all of the complexes listed in Table I are reduced to platinum(II) complexes following the same pattern as that found for complexes previously studied,[1] *i.e.*:

$$\textit{trans}\text{-}[PtL_2X_4] + 2Y^{n-} \longrightarrow \textit{trans}\text{-}[PtL_2X_2] + Y_2^{(2n-2)-} + 2X^- \qquad (3)$$

$$\textit{trans}\text{-}[PtL_2X_2] + 2Y^{n-} \longrightarrow \textit{trans}\text{-}[PtL_2Y_2]^{(2n-2)-} + 2X^- \qquad (4)$$

As far as reactions of the corresponding chloro- and bromo-complexes with the same reagent are concerned, it was found previously for platinum(IV) complexes with phosphine and arsine that the free energy of activation is 5.5 kcals/mole lower for the reactions of the bromo-complexes.[3] A value of about the same magnitude is found for the S-bonded and N-bonded complexes reported in Table I. This indicates that a

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(7) L. Cattalini, U. Belluco, R. Ettorre and M. Martelli, *Gazz. Chim. Ital.*, *94*, 356 (1964).

significant change in the nature of the uncharged ligand L has little effect in differentiating the ability of coordinated chloride and bromide to act as electron mediators.

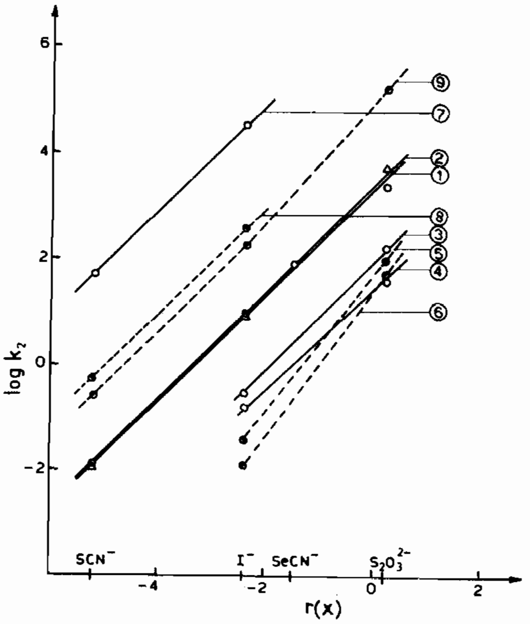

Figure 1. Correlation between log k_2, for reduction reactions of platinum(IV) complexes in methanol, at 40°C, and r(X)[2]. (For numerals, see Table I).

Figure 1 shows that, except for complexes with primary amines, the N-bonded and S-bonded complexes investigated obey the linear free energy relationship (1), previously found for P-bonded and As-bonded complexes.[4] This indicates that the same oxidation-reduction mechanism is involved for all these substrates. Data reported in Table I together with other data previously reported[1-4] show that the changes of reactivity of the different substrates towards the same reducing agent are mainly determined by changes in enthalpy of activation, the entropies of activation being nearly constant for the various complexes, within the experimental errors. The only relevant exceptions to this general behaviour are observed in the case of the complexes with primary amines, which do not obey relationship (1) (see Figure 1) and have entropies of activation much more positive than those found for the other complexes. This anomalous behaviour cannot be related to the nature of the coordinating atom (*i.e.* nitrogen). In fact other complexes containing N-bonded ligands, such as pyridine and piperidine, display a normal behaviour. It must be pointed out, however, that NH_2R ligands differ from the other ligands used, in having two hydrogen atoms linked to the coordinating atom. Therefore, hydrogen bonding between NH_2 groups and neighbouring molecules is expected to occur to some extent. This is supported by the appreciable solubility of *trans*-[$Pt(NH_2R)_2Cl_4$] in water.[8] Thus, hydrogen bonding with solvent molecules, and possibly with the incoming reducing anion, as well as different steric requirements for these complexes, can account for the observed discrepancies.

The values of the relative reactivity, r_s, of the different tetrachloro-complexes, calculated from relationship (1), can be conveniently chosen as a measure of the relative influence of the ligand L upon the rate of reduction of platinum(IV) complexes. In Table II the values of r_s for the tetrachloro-derivatives investigated (except for L = NH_2R), together with other derived from data of previous papers,[2-4] are reported.

Table II. Relative reactivities, r_s, of platinum(IV) complexes of the type *trans*-[PtL_2Cl_4] towards reduction.

Ligand L	r_s	Ligand L	r_s
$As(C_2H_5)_3$	-0.4 [a]	pip	1.95
$P(C_3H_7)_3$	0.0 [b]	$S(C_2H_5)_2$	3.35
$P(C_2H_5)_3$	0.2 [a]	$S(CH_3)_2$	3.4
py	1.5		

[a] Value taken from references 1 and 4. [b] Value taken from reference 2.

It is apparent, from the figures shown in Table II, that the π-bonding ability of the ligand L is not the only factor determining the difference of lability of platinum(IV) complexes towards reduction, as previously suggested[1] from the fact that [$Pt(diars)_2Cl_2$]$^{2+}$ (diars = o-phenylenebisdimethylarsine) is reduced with a rate higher than [$Pt(en)_2Cl_2$]$^{2+}$ (en = ethylendiamine). In fact the r_s values of complexes with amines, which are poor or no π acceptor ligands, are intermediate between r_s values of complexes with phosphine and thioethers, which are good π acceptors.

These results can be explained by assuming that the reactivity of platinum(IV) complexes towards reduction increases as the π-acceptor ability of the ligand L increases and as the σ-donor ability of this ligand decreases. Thus, the net balance of σ-withholding of electrons, which should favour the reactivity in the order $P<S<N$,[9] and of π-withdrawal of electrons, which should favour the reactivity in the order $N<P$, S,[9] makes the observed order of reactivity, *i.e.* $P<N<S$.

It may be noted that the change of ligand L is also responsible for changes of the oxidation-reduction potentials of systems of the type [PtL_2Cl_4]–[PtL_2Cl_2]. Ahrland and Chatt pointed out that a good oxidizing ability of [PtL_2Cl_4] is determined both by a good π-acceptor ability and by a poor σ-donor ability of the ligand L.[10] Thus, we can conclude that the role played by these factors in increasing the electron-affinity of the central atom determines both the oxidizing power and the reactivity towards reduction of [PtL_2Cl_4] complexes. However, the relative importance of σ and π effects in the activated complex of the oxidation-reduction process is probably not the same as in the complexes in their ground states. This can account for the difference between the reactivity order of Table II (namely $P<N<S$) and the oxidation-reduction potential order ($P<S<N$).[10]

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(8) H. D. K. Drew and H. J. Tress, *J. Chem. Soc.*, 1212 (1935).

(9) F. Basolo and R. G. Pearson, «Mechanism of Inorganic Reactions», J. Wiley, N. Y., p. 375 (1967).

(10) S. Ahrland and J. Chatt, *J. Chem. Soc.*, 1379 (1957).