Kinetics of Anation in Platinum(II) and Palladium(II) Complexes of N-Alkylated Diethylenetriamine *

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The kinetics of replacement of H_2O in the pseudo-octahedral complexes $[Pt(L\text{-}L\text{-}L)(H_2O)][ClO_4]_2$ (L-L-L = $Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$) and $[Pd(L\text{-}L\text{-}L)(H_2O)][ClO_4]_2$ (L-L-L = $R_2N[CH_2]_2NMe[CH_2]_2NR_2$, R = Me or Et] by the nucleophiles Cl^-, Br^-, I^-, $(NH_2)_2CS$, SCN^-, and $S_2O_3^{2-}$ have been studied in water at 25 °C. All the reactions exhibit a first-order dependence on both the substrate and the nucleophile concentration. The kinetic behaviour of the complexes depends markedly on the size of the substituents at the nitrogen atoms in the ligand L-L-L. When L-L-L = $Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$ the second-order rate constants follow the usual nucleophilicity scale and in the case of the platinum complex the kinetic behaviour can be related to that of the unhindered complex $[Pt(dien)(H_2O)]^{2+}$ (dien = $H_2N[CH_2]_2NH[CH_2]_2NH_2$). In the case of the palladium substrate where the ligand L-L-L bears four bulky ethyl groups the reactivity is largely reduced with respect to that where L-L-L = $Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$ and the usual scale of nucleophilicity is no longer valid. The experimental findings are interpreted in terms of the usual bimolecular attack at the metal on the basis of the electrophilicity and the steric hindrance at the reaction centre caused by the substituents of the tridentate ligand.

Increasing steric hindrance in platinum(II) and palladium(II) complexes [1] $[M(L\text{-}L\text{-}L)X]^+$ caused by alkyl substituents at the nitrogen atoms of a co-ordinated $H_2N[CH_2]_2NH[CH_2]_2NH_2$ (dien) ligand L-L-L leads to a large decrease of the rate constants k_1 and k_2 in the two-term rate law for replacement of X. In the so-called pseudo-octahedral complexes [2,3] (L-L-L = $R_2N[CH_2]_2NR'[CH_2]_2NR_2$, R = Et, R' = H; R = Me or Et, R' = Me; M = Pt or Pd, and X = Cl or Br) the nucleophile-dependent term k_2 disappears and the rate of replacement of the group X is controlled by the solvolytic path. Many studies,[4] including measurements of the activation volumes for solvolysis of some of these substrates, have shown that the term k_1 refers to a bimolecular attack of the solvent at the reaction centre; the predominance of k_1 in the two-term rate law can, therefore, be interpreted by considering the solvent as a more favoured nucleophile, with respect to the entering group.

Although there are scattered reports [5,6] that the steric hindrance brought about by alkyl substitution of dien is not sufficient to prevent the approach of a nucleophile to the central metal, the best way to determine the existence of a reagent-dependent path for pseudo-octahedral complexes is to study their anation reactions. A kinetic investigation on the substitution of H_2O in the complex $[Pd(L\text{-}L\text{-}L)(H_2O)]^{2+}$ (L-L-L = $Et_2N[CH_2]_2NH[CH_2]_2NEt_2$) has already been performed;[3] the dependence of the rate constants on the nucleophile concentration was interpreted in terms of an ion-pair mechanism. In order to shed further light on this matter we have studied the anation reactions of the complexes $[Pt(L\text{-}L\text{-}L)(H_2O)][ClO_4]_2$ (L-L-L = $Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$) and $[Pd(L\text{-}L\text{-}L)(H_2O)][ClO_4]_2$ (L-L-L = $R_2N[CH_2]_2NMe[CH_2]_2NR_2$, R = Me or Et) with the nucleophiles Cl^-, Br^-, I^-, SCN^-, $S_2O_3^{2-}$, and $(NH_2)_2CS$ in water at 25 °C.

Experimental

Materials—The complexes $[Pd(L\text{-}L\text{-}L)Cl]ClO_4$ (L-L-L = $R_2N[CH_2]_2NMe[CH_2]_2NR_2$, R = Me or Et) were prepared by the methods reported in the literature.[2] The salt $[Pt(L\text{-}L\text{-}L)Cl]ClO_4$ (L-L-L = $Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$) was prepared starting as follows. To Zeise's salt, $K[Pt(C_2H_4)Cl_3]$ (1 g), dissolved in water (30 cm^3) was added dropwise a stoicheiometric amount of freshly distilled ligand in water (10 cm^3). A yellow precipitate forms as soon as each drop of ligand is added and redissolves immediately. When the ligand addition was complete the solution was left under magnetic stirring for about 1 h. A white precipitate, which analyzed for the required product, formed (yield 90%) when a large excess of $NaClO_4$ was added to the solution. It was washed with cold water and ethanol. The substrate is conveniently crystallised from hot water. The complexes $[Pd(L\text{-}L\text{-}L)(H_2O)][ClO_4]_2$ and $[Pt(L\text{-}L\text{-}L)(H_2O)][ClO_4]_2$ (L-L-L = $Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$) were prepared by treating the respective chloroderivatives with $AgClO_4$ in water. To this end a weighed amount of complex was dissolved in a known quantity of water; the stoicheiometric amount of $AgClO_4$ was added and the solution was left in the dark under magnetic stirring until the precipitation of AgCl was complete. Silver chloride was then filtered off and the solution of the resulting $[M(L\text{-}L\text{-}L)(H_2O)][ClO_4]_2$ was appropriately diluted. In the case of the palladium(II) derivatives, precipitation of AgCl was almost immediate; with the platinum complex the reaction was very slow and it took over 2 months at room temperature for the solution of the complex and $AgClO_4$ to be free from silver ions. No attempt was made to isolate the aquo-complexes as pure compounds and the $[M(L\text{-}L\text{-}L)(H_2O)]^{2+}$ solutions were used directly for kinetic experiments. The compounds NaCl, NaBr, NaI, NaSCN, $Na_2S_2O_3$, and $(NH_2)_2CS$ were of reagent grade.

Kinetics.—All the kinetics were followed spectrophotometrically. When the reactions were slow enough to be studied

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* *Supplementary data available* (No. SUP 23437, 6 pp.): pseudo-first-order rate constants. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

by conventional spectrophotometry a Cary 219 or a Beckman D.U. spectrophotometer equipped with a Servogor S potentiometric recorder was used. Faster reactions were monitored by means of a Durrum-Gibson D-110 stopped-flow apparatus; the exponential changes of absorbance with time were displayed on a Gould Advance 054100 storage oscilloscope and then recorded on a Radiometer REC 61 potentiometric recorder. All the kinetic runs were performed under pseudo-first-order conditions with respect to the complex; at least five different concentrations were used for each nucleophile. The ionic strength of the solutions was maintained constant at 0.1 mol dm^{-3} by the addition of the appropriate amount of $NaClO_4$. In order to avoid acid dissociation of the substrates [2] both the complex and the nucleophile solutions were made acidic by means of $HClO_4$ so that, immediately after mixing, the pH of the reaction mixture was between 3.7 and 4.0. The values of the observed rate constants, $k_{obs.}$, obtained from the slopes of the usual plots of ln $(A_\infty - A_t)$ *vs.* time, where A_∞ is the absorbance after five to six half-lives and A_t the absorbance at time t, were reproducible to better than ±5%.

Results and Discussion

The fact that most of the reactions proceed only in one step and that the spectra of the reaction products are comparable with those of authentic samples, under the same experimental conditions, provides evidence that the process monitored is always that of anation [equation (1)]. In some cases, on using

$$[M(L\text{-}L\text{-}L)(H_2O)]^{2+} + Y^{n-} \longrightarrow [M(L\text{-}L\text{-}L)Y]^{(2-n)+} + H_2O \quad (1)$$

large concentrations of the nucleophiles $S_2O_3^{2-}$ or $(NH_2)_2CS$, a second reaction was observed; this process, probably corresponding to substitution of the chelate ligand L-L-L, was much slower than the first one and was not investigated. The values of the observed rate constants $k_{obs.}$ for all the reactions studied conform to the rate equation (2). This result

$$k_{obs.} = k_2[Y] \quad (2)$$

shows unambiguously that, when solvolysis cannot occur, the substitution reactions of the pseudo-octahedral complexes proceed entirely *via* a nucleophile-dependent path.

The values of k_2, obtained by least-squares analysis of plots of $k_{obs.}$ *vs.* [Y], are listed in the Table together with those relative to the reactions of the substrates $[Pt(L\text{-}L\text{-}L)(H_2O)]^{2+}$ (L-L-L = $R_2N[CH_2]_2NR'[CH_2]_2NR_2$; R = H, R' = H or Me) and $[Pd(L\text{-}L\text{-}L)(H_2O)]^{2+}$ (L-L-L = $Et_2N[CH_2]_2NH[CH_2]_2NEt_2$). The data indicate that the kinetic behaviour of the complexes $[M(L\text{-}L\text{-}L)(H_2O)]^{2+}$ depends strongly on the number and the size of the substituents at nitrogen in the chelate L-L-L. Not only the reactivity toward a given reagent but also the order of effectiveness of the entering group varies along the series of complexes.

In the case of $[M(L\text{-}L\text{-}L)(H_2O)]^{2+}$ (M = Pt or Pd, L-L-L = $Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$) the kinetic behaviour seems to conform to the general trend exhibited by palladium(II) and platinum(II) complexes. The k_2 values follow the usual nucleophilicity scale, *i.e.* $S_2O_3^{2-} > SCN^- > I^- > Br^- > Cl^-$. The availability of kinetic data for the unhindered complexes $[Pt(L\text{-}L\text{-}L)(H_2O)]^{2+}$ (L-L-L = $H_2N[CH_2]_2NR'[CH_2]_2NH_2$; R' = H [7] or Me [8]) allows a direct comparison with our substrate with L-L-L = $Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$. Such a comparsion can be conveniently made on the basis of the relation [9] (3) where log k_s is the

$$\log k_2 = \log k_s + s n_{Pt}^0 \quad (3)$$

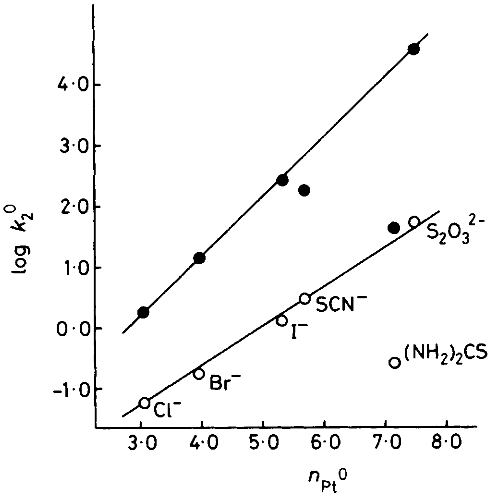

Figure. Plots of the rates of reaction of the complexes $[Pt(L\text{-}L\text{-}L)(H_2O)]^{2+}$ against n_{Pt}^0 for different nucleophiles. L-L-L = dien (●) (data from ref. 7) or $Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$ (○)

intrinsic reactivity, *i.e.* the logarithm of the rate constant for reaction of the complex with the poorest nucleophile (the solvent), s is the nucleophilic discrimination factor and represents the ability of a given substrate to discriminate among different nucleophiles, and n_{Pt}^0 is a set of nucleophilic reactivity constants determined for the complex *trans*-$[Pt(py)_2Cl_2]$ (py = pyridine). The discriminating ability of the three complexes decreases in the order L-L-L = $H_2N[CH_2]_2NH[CH_2]_2NH_2 > H_2N[CH_2]_2NMe[CH_2]_2NH_2 > Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$, the values of s * being 0.99 ± 0.05, 0.94 ± 0.02, and 0.69 ± 0.05 respectively. Furthermore, from the k_2 values in the Table, it can be seen that the reactivity of these substrates follows the same sequence. The Figure, where for the sake of clarity only two complexes are reported, shows that the biphilic reagent thiourea reacts much more slowly than expected on the basis of the n_{Pt}^0 values. The deviation of biphilic entering groups such as $(NH_2)_2CS$ and SCN^- from the n_{Pt}^0 scale in the reaction with $[Pt(dien)(H_2O)]^{2+}$ has been attributed [7] to the presence of the 2+ charge which reduces the availability of non-bonding electrons on the metal. It is noteworthy, however, that in the case of the present substrates no deviation is observed for the reaction with SCN^-; likewise, the deviation of thiourea is largely reduced with respect to the complex $[Pt(dien)(H_2O)]^{2+}$. The kinetic behaviour of the three complexes $[Pt(L\text{-}L\text{-}L)(H_2O)]^{2+}$ fits into a unified picture if we take into account the influence of the substituents at nitrogen on the electrophilicity of platinum. In the substrates $[Pt(L\text{-}L\text{-}L)(H_2O)]^{2+}$ (L-L-L = $R_2N[CH_2]_2NMe[CH_2]_2NR_2$, R = H or Me) the methyl groups increase the σ-donor properties of the ligand L-L-L and, consequently, decrease the electrophilicity of platinum with respect to $[Pt(dien)(H_2O)]^{2+}$. This effect is particularly relevant for the complex in which the ligand L-L-L bears five methyl substituents. The reduced electrophilicity of the reaction centre in this complex with respect to the others can explain the decrease in its capability to discriminate among the various nucleophiles as well as its reduced reactivity. In fact, in this case the formation of a fifth bond with the incoming group is disfavoured. Likewise, the electron density transmitted by the ligand $Me_2N[CH_2]_2$-

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* The values of log k_2 referring to the biphilic nucleophiles SCN^- and $(NH_2)_2CS$ have not been considered in the evaluation of s.

Table. Second-order rate constants k_2/dm^3 mol^{-1} s^{-1} for reaction of the complexes $[M(L-L-L)(H_2O)]^{2+}$ with various nucleophiles Y in water at 25 °C unless otherwise stated

M = Pt				M = Pd			
L-L-L	Y	k_2 [a]	k_2^0 [b]	L-L-L	Y	k_2 [a]	k_2^0 [b]
dien [c]	Cl^-	0.626 ± 0.011	1.93	$Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$ [d]	Cl^-	603 ± 8	1 860
	Br^-	4.64 ± 0.13	14.3		Br^-	904 ± 7	2 790
	I^-	80.6 ± 0.8	249		I^-	4 330 ± 35	13 400
	SCN^-	54.5 ± 1.6	168		SCN^-	12 000 ± 127	37 100
	$(NH_2)_2CS$	41.2 ± 0.6	41.2		$(NH_2)_2CS$	1 280 ± 29	1 280
	$S_2O_3^{2-}$	3 290 ± 10	37 400		$S_2O_3^{2-}$	28 000 ± 149	267 000
$H_2N[CH_2]_2NMe[CH_2]_2NH_2$ [d]	$Cl-$	0.336 ± 0.004	1.04	$Et_2N[CH_2]_2NMe[CH_2]_2NEt_2$ [d]	Cl^-	1.95 ± 0.03	6.03
	Br^-	1.98 ± 0.03	6.1		Br^-	1.33 ± 0.01	4.11
	I^-	57 ± 2.9	176		I^-	2.21 ± 0.01	6.82
	SCN^-	31.7 ± 0.3	98		$(NH_2)_2CS$	0.99 ± 0.011	0.99
	$(NH_2)_2CS$	23 ± 2.6	23		$S_2O_3^{2-}$	45.5 ± 0.9	434
$Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$ [d]	Cl^-	0.019 ± 0.001	0.059	$Et_2N[CH_2]_2NH[CH_2]_2NEt_2$ [e]	Cl^-		15.7
	Br^-	0.054 ± 0.003	0.167		Br^-		10.6
	I^-	0.374 ± 0.005	0.865		I^-		7.98
	SCN^-	0.92 ± 0.01	2.84		SCN^-		134
	$(NH_2)_2CS$	0.256 ± 0.007	0.256		$(NH_2)_2CS$		1.42
	$S_2O_3^{2-}$	5.51 ± 0.156	52.6		$S_2O_3^{2-}$		5 700

[a] $I = 0.1$ mol dm^{-3}. [b] Extrapolated to zero ionic strength using the relation $\log k_2 = \log k_2^0 + 1.02\, z_a z_b\, I^{\frac{1}{2}}(1 + I)^{-\frac{1}{2}}$ where z_a and z_b are the charges of the substrate and the nucleophile respectively. [c] From ref. 7; 30 °C. [d] From ref. 8. [e] From ref. 2.

$NMe[CH_2]_2NMe_2$ tends to compensate the positive charge on the metal allowing the reagents SCN^- and $(NH_2)_2CS$ to exert their biphilicity.

The kinetic behaviour of the complexes $[Pd(L-L-L)(H_2O)]^{2+}$ ($L-L-L = R_2N[CH_2]_2NR'[CH_2]_2NR_2$; R = Et, R′ = H or Me; R = R′ = Me) cannot be rationalised only in terms of electrophilicity of the reaction centre since this should be similar on the basis of the number and the nature of the groups bound to nitrogen in L-L-L. Nevertheless, the k_2 values show that both the reactivity and the discriminating ability of the substrates decreases progressively on going from $L-L-L = Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$ to $Et_2N[CH_2]_2NH[CH_2]_2NEt_2$ and $Et_2N[CH_2]_2NMe[CH_2]_2NEt_2$. Furthermore, in the last two complexes the usual reactivity scale of the entering group is no longer valid

The facts that the anation reactions of $[Pd(L-L-L)(H_2O)]^{2+}$ ($L-L-L = Et_2N[CH_2]_2NH[CH_2]_2NEt_2$) have a nucleophile dependence and that the replacement of H_2O by I^- occurs more slowly than it does with Br^- and Cl^- have been interpreted by Goddard and Basolo[3] in terms of an interchange mechanism in which an ion pair between the complex and the ligand rapidly forms and then collapses to give the product. The rate equation for such a mechanism is as in equation (2) where k_2 is given by kK_{IP}, providing $k_{IP} \ll 1$. Here K_{IP} is the ion-pair formation constant, and k the rate constant for its collapse. Goddard and Basolo's interpretation, although not supported by evidence for ion-pair formation, is attractive. Nevertheless, in the light of the new kinetic data presented here, and on the reasonable assumption that all the reactions of the complexes $[Pd(L-L-L)(H_2O)]^{2+}$ proceed by the same mechanism, it is difficult to explain the reactivity differences among the various substrates in terms of Basolo's model. In fact, if the ionic strength and the charges of the interacting ions are kept constant, the main factor determining the ion-pair formation constant is the distance of closest approach of these ions.[10] This parameter should be very similar for all the $[Pd(L-L-L)(H_2O)]^{2+}$ complexes and a given anionic nucleophile. Likewise, the rate constant k for the collapse of the ion pairs should not vary substantially with the nature of L-L-L. The observed reactivity decrease with L-L-L as well as the change in the entering-group sequence cannot therefore be explained by the ion-pair model.

More simply, the kinetic behaviour of the substrates $[Pd(L-L-L)(H_2O)]^{2+}$ can be interpreted in terms of the usual mechanism of substitution at square-planar complexes on the basis of steric hindrance at the central atom. The observed rate equation is in fact compatible with a direct bimolecular attack at the metal; the lack of a term independent of the nucleophile concentration is obviously due to the fact that the leaving group coincides with the solvent. Molecular models have shown[2] that in palladium(II) complexes containing the present $R_2N[CH_2]_2NR'[CH_2]_2NR_2$ ligands, the alkyl groups which are located below and above the square plane shield to some extent the reaction centre. In the complex $[Pd(L-L-L)X]^+$ ($L-L-L = Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$), where some vacant space is available for entry of a nucleophile, the second-order rate constants k_2 for the various anation reactions follow the usual nucleophilicity scale. However, in the complexes with the more bulky chelates $Et_2N[CH_2]_2NR'[CH_2]_2NEt_2$ (R′ = H or Me) the larger shielding of the central metal prevents the entering groups from exerting their whole potential nucleophilicity unless specific steric requirements are fulfilled. To be a good entering group a nucleophile must have a size compatible with the free space available around the central atom. Thus, the poor nucleophile Cl^- is a better entering reagent than I^-, which is more nucleophilic but bulkier.

An analogous interpretation[6] has been given to explain the relative rates of replacement of X, by various nucleophiles, in the substrates $[Pd(L-L-L)X]^+$ ($L-L-L = Et_2N[CH_2]_2NH[CH_2]_2NEt_2$; X = Cl, Br, I, N_3, SCN, or NCS). Here the solvolytic path is dominant and by using large entering-group concentrations it is possible to demonstrate nucleophile dependence of the rate of reaction. However, the second-order rate constant for entry of N_3^- is apparently much larger than it is for Br^- and I^-.

It seems therefore that for sterically hindered complexes of the type $[M(L-L-L)X]^{n+}$ (M = Pt or Pd; $L-L-L = R_2N[CH_2]_2NR'[CH_2]_2NR_2$; X = Cl, Br, I, N_3, H_2O, *etc.*) the replacement of the group X generally occurs by the usual associative mechanism. Owing to the steric crowding around the metal, the customary nucleophilicity scale for square-planar complexes is not obeyed. While very strong nucleophiles such as $S_2O_3^{2-}$ or SCN^- can overcome this steric barrier by way of their nucleophilic strength, poor nucleophiles such as N_3^- or Cl^- penetrate the metal shielding only because of their reduced size. In many cases, bulky entering groups, even when strongly nucleophilic, are less effective than small ligands having poor nucleophilicity.

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