Comparison of Uni- and Bi-dentate Ligands as Entering Groups in Some Reactions of 2,2′-Bipyridyldichloroplatinum(II)

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Second-order rate constants and activation parameters have been determined for the reactions in methanol of diethyl sulphide and several potentially bidentate ligands with the complex $Pt(bipy)Cl_2$(bipy = 2,2′-bipyridyl). The results are consistent with the suggestion made earlier that interactions in the transition state between one end of a bidentate group and a chlorine atom of the substrate are important in reactions of this type.

IN an earlier work [1] we reported a study of some reactions of uni- and bi-dentate amines with 2,2′-bipyridyldichloroplatinum(II). Compared with the reactions of the unidentate amines, those of the bidentate amines had more compact transition states (lower values of $\Delta H^‡$ and more negative $\Delta S^‡$) and these results were attributed to interactions between the bidentate entering groups and the chlorine atoms of the substrate. In the present work this effect is investigated further, with particular reference to entering groups containing sulphur as a donor atom.

EXPERIMENTAL

2,2′-Bipyridyl and 2-aminoethanol were Carlo Erba R.P. reagents; other ligands used were high-grade Schuchardt–Munchen reagents. The complex $Pt(bipy)Cl_2$ was prepared by the method of Morgan and Burstall.[2] General conditions for the kinetic experiments were as described previously.[1,3]

RESULTS

The spectra of mixtures of the complex $Pt(bipy)Cl_2$ and an excess of reacting ligand changed with time and showed well defined isosbestic points. Rate constants, k_{obs} (Table 1), were obtained from the gradients of plots of log $(A_t - A_\infty)$ against time t, where A_t and A_∞ are the absorbances, at a wavelength where large changes occurred, at time t and at the end of the reaction respectively.

Values of the rate constant k_2 (Table 2) were obtained from straight-line plots of k_{obs} against the ligand concentration. The intercepts of these lines at zero ligand concentration were small and could not be measured precisely. Activation parameters for the reactions are given in Table 2; those for ligands (IV) and (V) were calculated from values of $k_2/2$.

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[1] L. Baracco, L. Cattalini, J. S. Coe, and E. Rotondo, *J. Chem. Soc.* (*A*), 1971, 1800.

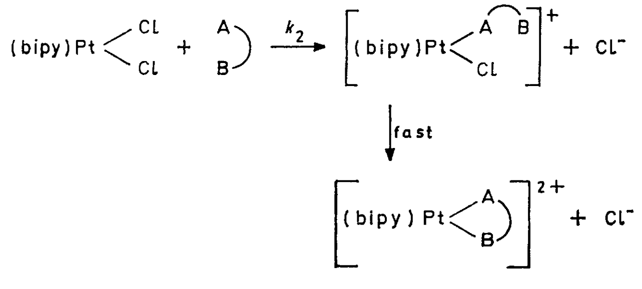
[2] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1934, 965.

[3] L. Cattalini, A. Orio, and A. Doni, *Inorg. Chem.*, 1966, **5**, 1517.

Reactions were also carried out on a preparative scale and the product complex cations were precipitated as their chloride or tetraphenylborate salts. Analytical data for these products are given in Table 3.

DISCUSSION

The present reactions show general similarities (spectral changes, kinetic form, and nature of the products) to the reactions of the complex $Pt(bipy)Cl_2$ with amines reported previously.[1] Thus the reactions occurring are probably those indicated below, where AB represents one of the bidentate ligands (I)—(V).



The reaction of $S(Et)_2$ (VI) with $Pt(bipy)Cl_2$ at 25 °C has been investigated previously.[4] The present measurements give fair confirmation of the earlier experiments and extend them to other temperatures. For entering groups (I) and (II), values of k_2 at a given temperature are similar and equal to about half the corresponding value for (V). We conclude from this that, for (I) and (II), displacement of the first Cl^- from the substrate results from attack by the sulphur atom of the entering group. In the case of 2-aminoethanol (III) the value of k_2 at 25 °C is about half that found previously for the reaction of ethylenediamine,[1] suggesting that the first stage of the reaction of 2-aminoethanol involves attack by the nitrogen atom. Thus, in each case, the rate-determining step involves attack by the softer of the two

TABLE 1

Observed rate constants (s^{-1}) for the reactions of ligands (L) with the complex $Pt(bipy)Cl_2$ in methanol; [L] = molar concentration of ligand

L		10 °C		25 °C		40 °C	
		[L]	10^4k_{obs}	[L]	10^4k_{obs}	[L]	10^4k_{obs}
(I)	$HS{\cdot}[CH_2]_2{\cdot}NMe_2,HCl$	0·165	6·2	0·143	12·2	0·142	25·9
		0·142	5·75	0·122	10·8	0·111	23·0
		0·106	5·2	0·092	9·8	0·095	21·0
		0·071	3·85	0·061	8·6	0·071	19·4
(II)	$HS{\cdot}[CH_2]_2{\cdot}NH_2,HCl$	0·229	4·82	0·229	9·90	0·234	28·9
		0·172	3·64	0·172	7·10	0·176	23·3
		0·114	2·87	0·114	4·90	0·117	19·2
		0·076	2·30	0·076	3·70	0·078	14·7
(III)	$HO{\cdot}[CH_2]_2{\cdot}NH_2$	0·0101	63·2	0·0277	224	0·0101	748
		0·0076	47·9	0·0208	174	0·0076	652
		0·00505	35·4	0·0138	132	0·00505	442
		0·0034	23·9	0·0092	115	0·0034	345

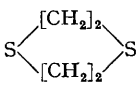
		15 °C		25 °C		32 °C		40 °C	
		[L]	10^4k_{obs}	[L]	10^4k_{obs}	[L]	10^4k_{obs}	[L]	10^4k_{obs}
(IV)		0·052	32·6	0·052	65·2	0·032	83·0	0·038	111
		0·043	27·4	0·040	55·4	0·024	59·0	0·032	92·0
		0·031	20·5	0·034	46·0	0·016	41·0	0·025	74·4
		0·026	16·3	0·026	34·7	0·0080	24·0	0·019	60·2
		0·017	12·6	0·017	24·9	0·0032	11·5	0·013	44·0
(V)	$HS{\cdot}[CH_2]_2{\cdot}SH$	0·600	28·3	0·684	65·4			0·600	152
		0·449	22·0	0·513	43·0			0·449	106
		0·299	15·8	0·342	33·3			0·299	80·6
		0·200	8·9	0·228	22·8			0·200	51·8
(VI)	SEt_2	0·421	230	0·484	585			0·800	1920
		0·315	179	0·404	460			0·600	1150
		0·211	132	0·242	264			0·400	960
		0·131	93·5	0·194	207			0·270	595
				0·161	180				

TABLE 2

Second-order rate constants and activation parameters[a] for the reactions of ligands (L) with the complex $Pt(bipy)Cl_2$ in methanol

	10^2k_2/l mol^{-1} s^{-1}				$\Delta H^‡$	$\Delta S^‡$
L[b]	10 °C	15 °C	25 °C	40 °C	kcal mol^{-1}	cal K^{-1} mol^{-1}
(I)	0·17		0·47	1·2	10·9	−33
(II)	0·16		0·39	0·92	9·7	−37
(III)	0·58		2·25	7·3	14·3	−18
(IV)[c]		6·0	12·0	27·0	10·1	−31
(V)		0·466	0·95	2·5	11·5	−31
(VI)		4·8	10·0	24·0	10·9	−27

[a] Calculated using a least-squares analysis; uncertainties are $\Delta H^‡ \pm$ *ca.* 0·5 kcal mol^{-1} and $\Delta S^‡ \pm$ *ca.* 2 cal K^{-1} mol^{-1}. [b] See Table 1 for key. [c] 10^2k_2 at 32 °C = 18·0 l mol^{-1} s^{-1}.

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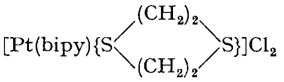
[4] L. Cattalini, M. Martelli, and G. Kirschner, *Inorg. Chem.*, 1968, **7**, 1488.

nucleophiles, in accord with the general expectation for reactions of a Pt^{II} substrate.

However, the activation parameters for the 2-aminoethanol reaction are rather similar to those found previously[1] for reactions of unidentate amines. This suggests, on the basis of our earlier interpretation, that the OH group of 2-aminoethanol is not strongly anchored in the transition state. For the reactions of the other ligands reported here comparison of the activation parameters shows that $\Delta H^\ddagger$ is slightly greater for unidentate $S(Et)_2$ than for the bidentate entering groups, and that the $\Delta S^\ddagger$ values become progressively more negative in the order (VI), (IV), (V), (I), and (II). These effects, reflecting an increased compactness of the transition states for the bidentate amines as compared with $S(Et)_2$, are not so clear cut as in the earlier comparison of bi- with uni-dentate amines. If the effects are mainly due to hydrogen-bonding interactions in the transition state between one end of the bidentate entering group and one of the chlorine atoms of the substrate, then the trend noted above may be rationalised in terms of variations in the nature of the interacting groups (*i.e.* differences in donor atoms, in the numbers of hydrogen atoms and lone pairs of electrons, and in steric effects). This supports the conclusion reached previously[1] that hydrogen bonding in this type of reaction is more important than interactions between the metal and the second donor atom of the entering group. When, as in some of the present examples [ligands (I), (IV), and (V)], these interactions are not very strong, it is to be expected that the observed effects will be greater on $\Delta S^\ddagger$ than on $\Delta H^\ddagger$ values.

Table 3

Analyses of products of the reactions of ligands (L) with the complex $Pt(bipy)Cl_2$

			%			
L[a]	Product		C	H	N	S
(I)	$[Pt(bipy)\{S(CH_2)_2N(CH_3)_2\}]Cl$	Found:	35·4	3·9	8·9	6·1
		Calc.:	34·2	3·7	8·55	6·55
(II)	$[Pt(bipy)\{S(CH_2)_2NH_2\}]Cl$	Found:	30·8	3·3	8·9	7·1
		Calc.:	31·2	3·05	9·1	6·95
(III)	$[Pt(bipy)\{O(CH_2)_2NH_2\}]B(Ph)_4$	Found:	59·2	4·9	5·6	
		Calc.:	59·2	4·7	5·75	
(IV)	$[Pt(bipy)\{S(CH_2)_2S\}]$	Found:	32·8	3·0	4·7	11·1
		Calc.:	31·6	2·98	5·16	11·8
(V)	 $[Pt(bipy)\{S\overset{(CH_2)_2}{\underset{(CH_2)_2}{\diamond}}S\}]Cl_2$	Found:	32·6	2·7	6·4	14·3
		Calc.:	32·6	2·75	6·35	14·5

[a] See Table 1 for key.

We thank the Italian Council for Research (C.N.R., Rome) for financial support.

[2/1111 *Received, 17th May,* 1972]