The Unusual Substitution Behaviour of Terpyridylplatinum(II) Complexes

R. J. MUREINIK and M. BIDANI

Department of Inorganic & Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

Received October 14, 1977

The kinetics of the reactions of Pt(terpy)Cl$^+$ with various ligands were measured. The complex is approximately 10^3–10^4 times more reactive than its dien analogue. The relative reactivity order observed for the ligands studied differs from that expected on the basis of their n_{Pt}^0 values. These data are discussed in the light of the ability of aromatic ligands to enter into π-bonding with the metal, and of the biphilic properties of the incoming groups involved. Although each ligand obeys the usual two-term rate law common for square-planar substitution, $k_{obs} = k_1 + k_2[Y]$, the value of k_1 is not common to all the incoming groups. A mechanism is proposed to account for this departure from "classical" behaviour.

Introduction

The mechanism of substitution in square-planar complexes has been extensively studied, and the basic patterns of reaction for these species are very well defined [1–6]. Studies of the reactions of complexes of Pt(II), Pd(II) and Au(III) with the tridentate ligand diethylenetriamine (dien) and its derivatives have played a significant role in bringing the subject of square-planar substitution to its present degree of understanding [1–6]. These studies exploited the well-known greater stability of chelating ligands, compared to their monodentate analogues, to render three coordination sites inert to substitution, thus limiting the overall process under consideration to a single ligand replacement at only one bonding site. In view of the great attention paid to dien complexes, it is surprising to find that reactions of other tridentate systems have been essentially ignored. This paper presents the results of a kinetic study of substitution reactions of Pt(II) complexes of the tridentate ligand, 2,2′,6′,2″ terpyridyl (terpy), in which the five-

terpy
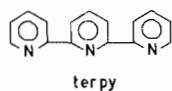
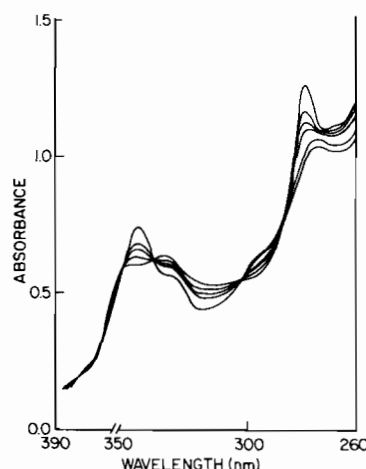membered chelate rings contain some unsaturated linkages. Considerable reactivity differences exist be-

Figure 1. Spectral changes during the reaction between Pt-(terpy)Cl$^+$ and SCN$^-$.

tween Pt(bipy)Cl$_2$, in which the chelate ring contains unsaturated bonds, and PtenCl$_2$, in which the chelate ring is saturated [7]. It was therefore of interest to compare the kinetics of the terpy and dien systems.

Experimental

The preparation and characterisation of the terpy complexes used in this study have been described elsewhere [8, 9]. Reaction products isolated under the conditions of the kinetic studies were identical with authentic samples of the same material. Analytical grade sodium salts were recrystallised from triply distilled water, which was used throughout. Ionic strength was controlled at 4.5 × 10^{-3} *M* with sodium perchlorate for the reactions with thiocyanate and nitrite, or sodium nitrate for the reactions with bromide and azide. Low total concentrations of ligand and ionic medium were necessary to avoid precipitation of the product before completion of the reaction, and this severely limited the concentration range in which the reactions could be studied. Kinetics were followed using a Perkin

TABLE I. Rate Constants for the Reaction of [Pt(terpy)Cl]$^+$ with Various Ligands[a].

Ligand	Temperature/K	10^3 k_1/s^{-1}	k_2/M s^{-1}
Br$^-$	283	6.16 ± 0.34	3.89 ± 0.12
	288	7.94 ± 0.31	5.42 ± 0.13
	293	10.43 ± 0.43	7.47 ± 0.14
	298[b]	12.5[b]	10.2[b]
SCN$^-$	298	1.08 ± 0.54	2.69 ± 0.16
	303	0.88 ± 0.32	4.86 ± 0.10
	308	0.52 ± 0.36	6.09 ± 0.13
NO$_2^-$	298	8.28 ± 0.36	2.66 ± 0.12
	303	9.99 ± 0.77	4.18 ± 0.26
	308	11.32 ± 0.87	5.78 ± 0.29
N$_3^-$	283	6.93 ± 0.81	6.37 ± 0.33
	288	6.73 ± 0.58	10.66 ± 0.27
	293	8.06 ± 0.83	13.35 ± 0.28
	298	12.41 ± 1.78	18.73 ± 0.70

[a]Error limits are one standard deviation. No added chloride.
[b]Extrapolated values.

TABLE II. Effect of the Leaving Group Concentration on the Rates of Reaction of Pt(terpy)Cl$^+$ with Nitrite[a].

Ligand	10^4 [Cl$^-$]/M	10^3 k_1/s^{-1}	k_2/M s^{-1}
NO$_2^-$	0.00	11.32 ± 0.87	5.78 ± 0.29
(T = 308K)	0.45	12.70 ± 1.13	4.49 ± 0.38
	0.90	12.60 ± 0.66	4.61 ± 0.21
	2.70	7.43 ± 0.43	5.17 ± 0.14
	4.50	4.52 ± 0.57	4.96 ± 0.22
	6.30	3.14 ± 0.22	5.27 ± 0.09
	9.00	0.97 ± 0.46	4.46 ± 0.19
	13.50	1.47 ± 0.24	4.41 ± 0.10
	18.00	0.81 ± 0.19	3.84 ± 0.97
			Mean = 4.77 ± 1.0

[a]Error limits are one standard deviation.

Elmer 402 spectrophotometer equipped with a thermostatted cell holder that enabled the temperature to be controlled to ±0.1 K. The spectral changes involved are all small (Figure 1), often being no more than 0.2 absorbance units, and five-fold absorbance scale expansion was employed throughout. Reactions were always conducted in a large excess of entering group to ensure pseudo-first order conditions.

Results

Repeated scanning of the spectrum of a solution of [Pt(terpy)Cl] Cl containing the appropriate amount of ligand shows the development of a number of well defined isosbestic points. A typical example is seen in Figure 1. Under the experimental condi-
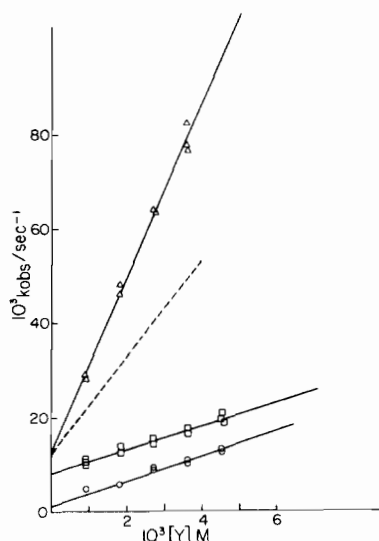

Figure 2. Dependence of k_{obs} on concentration of incoming ligand. ○ = SCN$^-$; □ = NO$_2^-$; △ = N$_3^-$; T = 298 K. The dotted line represents the calculated rate constants for bromide at 298K.

tions chosen all the reactions go to completion, and pseudo-first-order rate constants, k_{obs}, were obtained under various conditions from the slopes of graphs of log(A_t − A_∞) against time. In the absence of added chloride, the reactions of each ligand obey a two-term rate equation (1) of the form frequently encountered [1–5] in square-planar substitution

$$k_{obs} = k_1 + k_2[Y] \qquad (1)$$

Values of k_1 and k_2 are listed in Table I. However, as shown in Figure 2, the azide, nitrite and thiocyanate entering groups give different values of k_1, unlike the common pattern of behaviour in which the value of the intercept is independent of the nature of the incoming ligand [1–6]. The reaction of Pt(terpy)Cl$^+$ with bromide was not studied at 298K, and the dotted line is calculated for this temperature on the basis of extrapolated rate constants obtained from Arrhenius plots for this reaction.

The unusual solvent path behaviour prompted a more detailed study of the dependence of k_1 on the concentration of the leaving group [6, 10]. As can be seen in Table II, the addition of chloride in the reaction between the complex and nitrite ion causes k_1 to fall, whereas k_2 remains essentially unchanged. A rate equation of the form (1) continues to operate. The dependence of k_1 on [Cl$^-$] can be expressed as (2)

$$k_1 = 1/\{a[Cl^-] + b\} \qquad (2)$$

with a = 4.5 × 10^4 M^{-1} s and b = 60s.

For azide ion, considerable scatter and large standard deviations were observed in the k_1 path, and no systematic relationship could be detected between k_1

TABLE III. Activation Parameters at 298K for the Reactions of Pt(terpy)Cl$^+$ with Various Ligands.

Ligand	$\Delta H_1^{\ddagger}$/kJ mol^{-1}	$\Delta H_2^{\ddagger}$/kJ mol^{-1}	$\Delta S_1^{\ddagger}$/JK^{-1}	$\Delta S_2^{\ddagger}$/JK^{-1}
Br$^-$	30.6	42.3	−179	−84
SCN$^-$	−	58.4	−	−41
NO$_2^-$	22.0	58.0	−211	−42
N$_3^-$	39.6	46.5	−149	−64

and [Cl$^-$] within the experimental error. The value of k_2 was not affected by added chloride. Because of the small relative contribution of k_1 to the overall rate for the reaction of thiocyanate, these values are associated with considerable experimental error (which is probably responsible for the apparent anomalous temperature dependence noted in Table I for k_1). For this reason no attempt was made to study the systematic variation of k_1 with [Cl$^-$], although individual reactions were shown to proceed at the same rate in the presence of chloride as in its absence.

Activation parameters obtained from temperature dependence studies without added chloride are listed in Table III.

Discussion

Three main points of interest arise from the results described above: the considerably greater reactivity of the terpy substrate compared to its dien analogue, the unusual reactivity order in the ligand path N$_3^-$ > Br$^-$ > NO$_2^-$ > SCN$^-$, and the unusual behaviour of the k_1 path.

Reactivity of Terpy Complexes

The rates of reaction of PtdienCl$^+$ with the ligands used in this study have been reported by Cattalini *et al.* [11]. In all cases the terpy complex reacts some 10³–10⁴ times faster than the dien complex. Similar qualitative comparisons were previously noted for some reactions of terpy complexes with pyridine, but the subject was not pursued in any detail [12]. The reactions of PtbipyCl$_2$ with dithiooxamide are approximately 100 times faster than those of either PtenCl$_2$ or *cis*-Ptpy$_2$Cl$_2$ [7]. Since infrared studies [13] showed that the strength of the Pt–Cl bond is not much affected by the nature of the amine (and is in fact strongest in the bipy complex), labilisation of the ground state by the σ-*trans* effect is not responsible for the extreme increase in reactivity. No significant difference was found for ν(Pt–Cl) for the dien and terpy compounds [9]. Conrad and Rund [14] extended the study of the reactions of dithiooxamide with bipy complexes to include variously substituted bipy ligands. They suggested that labilisation occurs

by the π-*trans* effect in which the vacant π* molecular orbitals of bipy delocalised negative charge from the metal centre by overlap with the d_{xz} and d_{yz} orbitals of the platinum. In the series of complexes Pt(bipy)Cl$_2$ and its substituted derivatives, PtenCl$_2$ and *cis*-Ptpy$_2$Cl$_2$, only the bipy ligands can act in this way, since they are coplanar with the molecular plane and possess vacant π orbitals capable of the overlap. In *cis*-Ptpy$_2$Cl$_2$ the pyridine rings are not coplanar with the coordination plane and en is saturated.

Similar factors probably account for the reactivity of the terpy compounds. Although the exact structure of Pt(terpy)Cl$^+$ is not known, intuitively and by analogy with the structure of its palladium analogue [15], the tridentate ligand is expected to be almost rigorously coplanar with the coordination plane. Extensive delocalisation of electronic charge from the metal onto the amine is thus possible, and a π-*trans* effect probably operates. Although a direct comparison of PtbipyCl$_2$ and Pt(terpy)Cl$^+$ is probably not valid because of the different charge type and the different reaction media required, the tridentate complex appears to be more reactive than the bipy species in accordance with the greater possibility of π-interaction introduced by the third pyridine ring.

Reactivity of the Ligands

The reactivity index n_{Pt}^o of the various ligands towards square-planar substitution has been defined by the use of a standard complex *trans*-Ptpy$_2$Cl$_2$ as reference substrate. In this system the reactivity order is SCN$^-$ > Br$^-$ > N$_3^-$ > NO$_2^-$, which differs markedly from the reactivity order observed here in the k_2 path. Although reactivity orders towards other complexes usually follow the n_{Pt}^o sequence, inversion of this order is not infrequent. An early example is the greater reactivity of chloride (n_{Pt}^o = 3.04) than nitrite (n_{Pt}^o = 3.22) towards Ptdien(H$_2$O)$^{2+}$ [16] Cattalini *et al.* [11] showed that ligands in which electrophilicity is an important aspect of their "reactivity make-up", react significantly slower than expected on the basis of their n_{Pt}^o values with complexes containing groups able to delocalise negative charge away from the metal ion. On the other hand, anionic complexes in which the electron density on
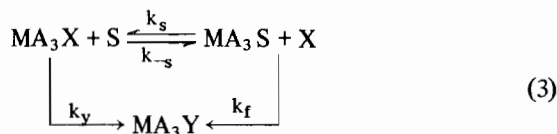
the metal is enhanced were more reactive than expected towards such incoming groups. Prominent among these "biphilic" agents were thiocyanate and nitrite.

Cattalini et al. [17, 18] showed that linear free energy relationships exist between the pK_a for the base in aminogold(III) complexes and the rate of reaction of the complex with ligands that do not possess electrophilic properties. However, these relationships break down for ligands such as NO_2^- and N_3^- in which electrophilicity is an important component of their reactivity.

In the present system two factors operate which reduce the ability of the ligands to exercise their electrophilic properties. The positive charge of the complex will tend to make electron density on the metal less available to incoming ligands possessing electrophilic characteristics [11]. Furthermore, although the ability of terpy to delocalise charge from the metal will increase the nucleophilic reactivity of the ligand and hence the overall reaction rate compared to systems in which such delocalisation cannot occur, this will also have the effect of changing the relative reactivity of those ligands for which electrophilicity is an important aspect of their mode of reaction. Thus the ligands SCN^- and NO_2^- are particularly affected and react considerably slower than Br^- and N_3^-. Azide and bromide do not differ by much in their n_{Pt}^o values, and a small shift in reactivity is sufficient to reverse their usual reactivity order, although it is not clear why azide should be as specifically active as was found or why the reactivity of bromide should be reduced by factors that should enhance nucleophilic attack.

Nature of the k_1 Path

The nature of the k_1 term in rate equations of the form (1) has recently been reviewed [6]. Frequently, simplified equations are observed in which one or other of the two terms is effectively zero. If the general mechanism of square-planar substitution is represented as
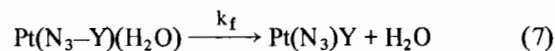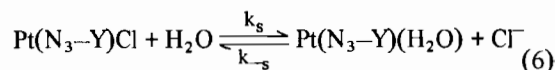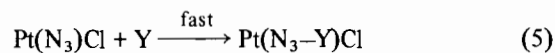
$$MA_3X + S \underset{k_{-s}}{\overset{k_s}{\rightleftarrows}} MA_3S + X$$
$$\Big\lfloor k_y \longrightarrow MA_3Y \overset{k_f}{\longleftarrow} \Big\rfloor \tag{3}$$

the overall kinetic expression is

$$k_{obs} = \frac{k_s k_f [Y]}{k_{-s}[X] + k_f[Y]} + k_y[Y] \tag{4}$$

Equation (4) will reduce to $k_{obs} = k_s + k_y[Y]$, *i.e.*, equation (1), when $k_{-s} [X] \ll k_f[Y]$, with all ligands yielding the same value of k_s since this is a property of the complex alone. Bekker and Robb [19] showed that different values of k_1 may be ob-

tained for different ligands if $k_{-s}[X] \sim k_f[Y]$, in which case $k_1 \sim \frac{1}{2} k_s$. However, in only one case has such behaviour been reported, and the mathematical analysis of the mechanism appears to be in error [20].

The dependence of k_1 on the nature of Y in the present system may derive from the above variation of the classical mechanism. However, another possibility is the intervention in the solvent path of a fast prior reaction incorporating the ligand into a species which subsequently undergoes rate-determining reaction. The following schematic mechanism* for the k_1 path, in which Pt(terpy)Cl$^+$ incorporates Y by a process other than the substitution of chloride by Y,

$$Pt(N_3)Cl + Y \xrightarrow{\text{fast}} Pt(N_3-Y)Cl \tag{5}$$

$$Pt(N_3-Y)Cl + H_2O \underset{k_{-s}}{\overset{k_s}{\rightleftarrows}} Pt(N_3-Y)(H_2O) + Cl^- \tag{6}$$

$$Pt(N_3-Y)(H_2O) \xrightarrow{k_f} Pt(N_3)Y + H_2O \tag{7}$$

yields the expression

$$k_1 = \frac{k_s k_f}{k_{-s}[Cl^-] + k_f} \tag{8}$$

which is of the same form as (2) with $a = k_{-s}/k_s k_f$ and $b = 1/k_s$.

Gillard et al. [21–23] have recently demonstrated that when pyridine derivatives are quaternised by coordination to metal ions, including Pt(II), addition of nucleophiles, particularly OH$^-$ groups, becomes possible at the carbon atoms α-to the heteronitrogen atom (9). Although the low solubility of the terpy

$$\tag{9}$$

complexes precludes nmr investigation of such addition phenomena, these complexes show behaviour similar to that of Pt(phen)$_2^{2+}$ [23], in keeping with the development of partial positive charge at the α-carbon atom. For example, addition of hydroxide to a solution of Pt(terpy)Cl$^+$ leads to spectral changes that are reversible on acidification. This reversibility eliminates the possibility of the spectral changes being due to base hydrolysis and is in keeping with the occurrence of a reaction of the type (9). Other evidence is discussed elsewhere [9].

Equation (5) of the proposed mechanism would thus entail addition of the incoming ligand at an α-carbon atom of terpy. After the usual solvolytic stage, migration of Y bound to the ligand to the coordination sphere (7), yields the final product.

---

*N_3 = terpy: charges omitted for clarity.

Of the ligands used in this study, bromide and azide behave "normally" in the sense that they share a common value for k_1 and that the solvent path for the azide reaction is not influenced by chloride concentration. A mechanism of the type (5 - 7) would explain the chloride dependence observed in the reaction with nitrite, and its operation would account for the different values found for k_1 for different ligands. However, the mechanism discussed above can only be regarded as speculative, since other formulations of $Pt(N_3-Y)Cl$, such as formation of a five-coordinate intermediate complex, will also account for the mathematical form of (2). The activation entropies for both paths are negative, as expected for associatively activated substitution [1–6], but the values of $\Delta S^{\ddagger}$ are much more negative than those in the ligand path. This is consistent with, but by no means constitutes verification of, a mechanism in which the solvent path involves a greater extent of association. However, in view of the complex nature of k_1, values of $\Delta H_1^{\ddagger}$, and $\Delta S_1^{\ddagger}$, describe complex processes, and their interpretation is not clear.

Further work on the mechanism of terpy complexes is called for, and our current efforts include attempts to synthesise terpy complexes that are sufficiently soluble for nmr study of the tentatively proposed addition reaction at the α-carbon atom.

Acknowledgements

References

1 F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions", 2nd Ed., Wiley, New York (1967) chap. 5.
2 C. H. Langford and H. B. Gray, "Ligand Substitution Processes", Benjamin, New York (1966) chap. 2.
3 L. Cattalini, *Prog. Inorg. Chem., 13,* 263 (1970).
4 L. Cattalini, in: *MTP International Review of Science, Inorg. Chem.,* Series One, Vol. 9, Ed. M. L. Tobe, p. 269.
5 M. L. Tobe, "Inorganic Reaction Mechanisms", Nelson, London (1972) chap. 5.
6 R. J. Mureinik, *Coord. Chem. Rev.,* in the press.
7 P. Haake and P. A. Cronin, *Inorg. Chem., 2,* 879 (1963).
8 G. T. Morgan and F. H. Burstall, *J. Chem. Soc.,* 1498 (1934).
9 R. J. Mureinik and M. Bidani, *Inorg. Nucl. Chem. Lett., 13,* 625 (1977).
10 R. J. Mureinik, *Inorg. Chim. Acta, 13,* 127 (1975).
11 L. Cattalini, A. Orio and M. Nicolini, *J. Am. Chem. Soc., 88,* 5734 (1966).
12 F. Basolo, H. B. Gray and R. G. Pearson, *J. Am. Chem. Soc., 82,* 4200 (1960).
13 T. Boschi, G. Deganello and G. Carturan, *J. Inorg. Nucl. Chem., 31,* 2423 (1969).
14 J. R. Conrad and J. V. Rund, *Inorg. Chem., 11,* 129 (1972).
15 G. M. Intille, C. E. Pflager and W. A. Baker, *J. Cryst. Mol. Struct., 3,* 47 (1973).
16 H. B. Gray and R. J. Olcott, *Inorg. Chem., 1,* 481 (1962).
17 L. Cattalini, A. Orio and M. L. Tobe, *Inorg. Chem., 6,* 75 (1967).
18 L. Cattalini and M. L. Tobe, *Inorg. Chem., 5,* 1145 (1966).
19 P. van Z. Bekker and W. Robb, *Int. J. Chem. Kin., 7,* 87 (1975).
20 C. G. Nicholson and W. Robb, *Inorg. Chim. Acta, 8,* 41 (1974).
21 R. D. Gillard and J. R. Lyons, *Chem. Comm.,* 546 (1973).
22 R. D. Gillard, *Coord. Chem. Rev., 16,* 67 (1975).
23 E. Bielli, R. D. Gillard and D. W. James, *J. Chem. Soc. Dalton,* 1837 (1976).