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# Reactivity of neutral nitrogen donors in square-planar $d^8$ metal complexes: The system chloro(2,2′:6′,2″-terpyridine)platinum(II) cation with five-membered N-donor heterocycles in methanol

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**Abstract**

The kinetics of the forward and reverse steps of the reaction $[Pt(terpy)Cl]^+ + nu \rightleftharpoons [Pt(terpy)(nu)]^{2+} + Cl^-$ (terpy = 2,2′:6′,2″-terpyridine, nu = one of a number of thiazoles, oxazole, isoxazole, imidazole, pyrazole and 3,5-dimethylpyrazole, covering a wide range of basicities) have been studied in methanol at 25 °C. Both forward and reverse reactions obey the usual two-term rate law observed in square-planar substitution. The second-order rate constants for the forward reactions, $k_2^r$, show a slight dependence upon the basicity of the entering nu, while the steric hindrance due to the presence of one methyl group in the α position to the nitrogen markedly decreases the reactivity. The second-order rate constants for the reverse reactions, $k_2^r$, are very sensitive to the nature of the leaving group and a plot of $\log k_2^r$ against the $pK_a$ of the conjugate acids of the unhindered five-membered N-donors is linear with a slope of −0.51. The results are compared with data from the literature regarding a series of pyridines reacting with the $[Pt(terpy)Cl]^+$ cation under the same experimental conditions. Both in the forward and in the reverse reaction, the reactivity depends not only upon the ligand basicity but also upon the nature of the nucleophile in the order: (thiazoles, oxazole, isoxazole, imidazole, pyrazoles) > pyridines for the entry of N-donors and on the contrary for the displacement by $Cl^-$. Steric retardation, due to the presence of a methyl group in the α position to the nitrogen, is remarkably lower for five-membered N-donors if compared to pyridines both in the forward and in the reverse reaction.


*Keywords:* Platinum; Kinetics; Five-membered N-donors; Heterocycles; Nucleophilicity

## 1. Introduction

As a part of a systematic study about the nucleophilicity and lability of neutral nitrogen donors towards square-planar four-coordinate complexes and the relationship between the reactivity and proton basicity, we have reported kinetic and equilibrium data concerning the reversible displacement of chloride by am (am = a number of pyridines and some heterocyclic and aromatic amines) from mono-cationic and bis-cationic complexes [1–4]. In all the cases, the kinetic behaviour is in accord with a reaction profile involving a transition state in which the Pt–Cl bond is almost completely formed, whereas the Pt–N bond is significantly weakened. As a consequence, the reactivity of entering pyridines and the other amines depends linearly and only slightly upon their basicity according to a linear free energy relationship of the type $\log k_2 = a(pK_a) + b$, where the parameters $a$ and $b$ take into account electronic and steric effects. On the other hand, the reverse reaction, the displacement by chloride of coordinated nitrogen donors from Pt(II) complexes, involves that am moves from a situation in which the Pt–N bond is completely

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formed to one in which it is greatly weakened. In this case, even if the lability of the amines is still linearly related to their basicity, the constant *b* for unhindered pyridines, that is their lability, is smaller than the one of other $sp^3$ aliphatic N-donors bases and evidences have been presented for a significant contribution of a π interaction between the filled d orbitals of the metal and the empty antibonding orbitals of the pyridine ring, that contributes to the stabilization of the ground state of the substrates. This suggestion seems to be in agreement with further deviations observed for pyridines having a *para*-substituent able to contribute to the π system [1,3]. In order to improve these experimental observations and the range of applicability of the proposed interpretation, we have now extended our study to five-membered nitrogen donors (thiazoles and isostructural species such as oxazole, isoxazole, imidazole and pyrazoles) by measuring the kinetics of the forward and reverse steps of the process (1).

$$[Pt(terpy)Cl]^+ + nu \rightleftharpoons [Pt(terpy)(nu)]^{2+} + Cl^- \quad (1)$$

(nu = thiazole, 4-methylthiazole, 4,5-dimethylthiazole, 5-methylthiazole, oxazole, isoxazole, imidazole, 3,5-dimethylpyrazole, pyrazole and only for the reverse reaction 2-aminothiazole and benzothiazole). The kinetics were carried out in methanol at 25 °C in order to directly compare the results with those obtained with other nitrogen donors under the same experimental conditions [3] and to widen and complete our precedent study regarding only two unhindered five-membered N-donors [5]. The great importance of ligand substitution reactions on $[Pt(terpy)L]^{n+}$ substrates is underlined by the recent publication of a number of papers regarding kinetics and mechanism of the reactions between biologically relevant ligands and the $[PtCl(terpy)]^+$ or $[Pt(H_2O)(terpy)]^{2+}$ cations [6–8].

## 2. Experimental

### 2.1. Materials

2,2′,6,2″-Terpyridine was purchased from Aldrich. Pure reagent-grade LiCl, $CH_3SO_3Na$, $CH_3SO_3H$, $AgClO_4$ (Aldrich) were used without further purification. The thiazoles, oxazole, isoxazole, imidazole and pyrazoles were recrystallized or distilled before use when necessary. Anhydrous MeOH was obtained by distillation over Mg wires, but traces of water did not appear to have any appreciable effect upon the reactions.

### 2.2. Instruments

Electronic spectra and kinetic measurements were obtained on a Perkin–Elmer Lambda 15 spectrophotometer. $^1$H NMR spectra were taken on Bruker Avance 300 or Bruker AC 200 spectrometers. Elemental analyses were performed by the Microanalytical Laboratory of the University of Padua.

### 2.3. Preparation of complexes

$[Pt(terpy)Cl]ClO_4$ was prepared starting from *cis*/*trans*-$[PtCl_2(SMe_2)_2]$ as reported in the literature [9].

All other complexes of the type $[Pt(terpy)(nu)](ClO_4)_2$ (nu = thiazole, 4-methylthiazole, 3,5-dimethylthiazole, 5-methylthiazole, $2NH_2$-thiazole, benzothiazole, oxazole, isoxazole, imidazole, pyrazole and 3,5-dimethypyrazole) were prepared as follows. $AgClO_4$ (0.103 g, 0.5 mmol) was added, under stirring in the dark, to a warm mixture (10 ml, 50 °C) of $[Pt(terpy)Cl]ClO_4$ (0.281 g, 0.5 mmol) in nitromethane. After 10 min, the AgCl formed was filtered off and the solution was treated with 0.5 mmol of the nitrogen ligand, stirred for 15 min and finally diethylether (50 ml) was added. The powdery product precipitated was filtered off, washed twice with diethylether and dried in vacuo. Yields >80% in all cases. Analytical and $^1$H NMR data for the complexes are collected in Tables 1 and 2, respectively.

$^1$H NMR for coordinated five-membered N-donors are given according to Scheme 1.

### 2.4. Kinetics

The reactions were initiated by adding a 0.05 mol $dm^{-3}$ dimethylformamide solution (2–20 μl) of the substrate complex, $[Pt(terpy)Cl]^+$ or $[Pt(terpy)(nu)]^{2+}$ to a methanolic solution (3 $cm^{-3}$) of the appropriate reagent, the nitrogen donor or chloride ion respectively, previously brought to the reaction temperature (25 °C) in a thermostatted cell in

Table 1
Analytical data

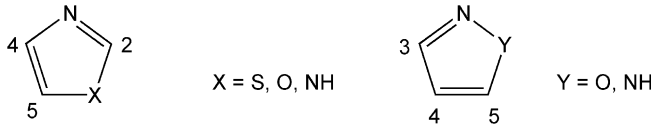
| Complex | Analysis[a] (%) | | |
|---|---|---|---|
| | C | H | N |
| $[Pt(terpy)Cl](ClO_4)$ | 31.7 (32.0) | 2.13 (1.97) | 7.41 (7.46) |
| $[Pt(terpy)(thiazole)](ClO_4)_2$ | 30.5 (30.3) | 1.84 (1.98) | 7.75 (7.86) |
| $[Pt(terpy)(4\text{-methylthiazole})](ClO_4)_2$ | 31.3 (31.4) | 2.07 (2.22) | 7.68 (7.71) |
| $[Pt(terpy)(4,5\text{-dimethylthiazole})](ClO_4)_2$ | 32.2 (32.4) | 2.38 (2.45) | 7.39 (7.57) |
| $[Pt(terpy)(5\text{-methylthiazole})](ClO_4)_2$ | 31.56 (31.42) | 2.02 (2.22) | 7.83 (7.71) |
| $[Pt(terpy)(2\text{-aminothiazole})](ClO_4)_2$ | 30.0 (29.7) | 2.14 (2.08) | 9.51 (9.63) |
| $[Pt(terpy)(benzothiazole)](ClO_4)_2$ | 35.6 (35.6) | 1.98 (2.21) | 7.12 (7.23) |
| $[Pt(terpy)(oxazole)](ClO_4)_2$ | 31.2 (31.0) | 2.24 (2.03) | 8.12 (8.05) |
| $[Pt(terpy)(isoxazole)](ClO_4)_2$ | 31.1 (31.0) | 2.17 (2.03) | 7.91 (8.05) |
| $[Pt(terpy)(pyrazole)](ClO_4)_2$ | 31.3 (31.1) | 2.22 (2.17) | 10.2 (10.1) |
| $[Pt(terpy)(3,5\text{-dimethylpyrazole})](ClO_4)_2$ | 32.9 (33.2) | 2.79 (2.65) | 9.52 (9.68) |
| $[Pt(terpy)(imidazole)](ClO_4)_2$ | 29.8 (31.1) | 1.87 (2.17) | 9.85 (10.1) |

[a] Calculated values in parentheses.

Table 2
$^1$H NMR[a] data of the complexes

| Compound | $^1$H NMR ($\delta$, ppm; $J$, Hz; $CD_3NO_2$, 298 K) |
|---|---|
| [Pt(terpy)(thiazole)](ClO$_4$)$_2$ | 9.85 (dd, 1H, $^4J_{H-H} = 2.2$, $^4J_{H-H} = 1.0$, $^3J_{Pt-H} = 22$, thiazole-H$_2$); 8.70–7.30 (m, 11H, terpy); 8.58 (dd, 1H, $^3J_{H-H} = 3.5$, $^4J_{H-H} = 1.0$, thiazole-H$_4$); 8.33 (dd, $^3J_{H-H} = 3.5$, $^4J_{H-H} = 2.2$, thiazole-H$_5$) |
| [Pt(terpy)(4-methylthiazole)](ClO$_4$)$_2$ | 9.75 (d, 1H, $^4J_{H-H} = 2.4$, $^3J_{Pt-H} = 22$, thiazole-H$_2$); 8.70–7.70 (m, 11H, terpy); 7.93 (dq, $^4J_{H-H} = 2.4$, $^4J_{H-H} = 1.2$, thiazole-H$_5$); 2.89 (d, 3H, $^4J_{H-H} = 1.2$, $^4J_{Pt-H} = 6$, thiazole-Me$_4$) |
| [Pt(terpy)(5-methylthiazole)](ClO$_4$)$_2$ | 9.60 (d, 1H, $^4J_{H-H} = 1.0$, $^3J_{Pt-H} = 22$, thiazole-H$_2$); 8.70–7.79 (m, 11H, terpy); 8.26 (qt, 1H, $^4J_{H-H} = 1.3$, $^4J_{H-H} = 1.0$, thiazole-H$_4$); 2.75 (d, 3H, $^4J_{H-H} = 1.3$, thiazole-Me$_5$) |
| [Pt(terpy)(2-aminothiazole)](ClO$_4$)$_2$ | 8.70–7.80 (m, 11H, terpy); 7.57, 7.12 (AB spin system, 2H, $^3J_{AB} = 4.3$, thiazole-H$_{4,5}$); 7.06 (s, br, 2H, thiazole-NH$_2$) |
| [Pt(terpy)(4,5-dimethylthiazole)](ClO$_4$)$_2$ | 9.50 (s, 1H, $^3J_{Pt-H} = 22$, thiazole-H$_2$); 8.70–7.30 (m, 11H, terpy); 2.80 (s, 3H, $^4J_{Pt-H} = 6$, thiazole-Me$_4$); 2.65 (s, 3H, thiazole-Me$_5$) |
| [Pt(terpy)(benzothiazole)](ClO$_4$)$_2$ | 10.15 (s, 1H, $^3J_{Pt-H} = 24$, thiazole-H$_2$); 8.86–7.34 (m, 15H, terpy + benzothiazole) |
| [Pt(terpy)(oxazole)](ClO$_4$)$_2$ | 9.28 (s, 1H, $^3J_{Pt-H} = 10$, thiazole-H$_2$); 8.80–7.20 (m, 13H, terpy+oxazole) |
| [Pt(terpy)(isoxazole)](ClO$_4$)$_2$ | 9.37 (d, 1H, $^3J_{H-H} = 2.2$, isoxazole-H$_3$); 9.30 (d, 1H, $^3J_{H-H} = 2.0$, isoxazole-H$_5$); 8.76–7.76 (m, 11H, terpy); 7.28 (dd, 1H, $^3J_{H-H} = 2.2$, $^3J_{AB} = 2.0$ Hz, isoxazole-H$_4$) |
| [Pt(terpy)(imidazole)](ClO$_4$)$_2$ | $^1$H NMR: 8.57 (t, 1H, $^4J_{H-H} = 1.8$, imidazole-H$_2$); 8.71–7.76 (m, 11H, terpy); 7.72 (dd, 1H, $^3J_{H-H} = 2.4$, $^4J_{H-H} = 1.8$, imidazole-H$_4$); 7.65 (dd, 1H, $^3J_{H-H} = 2.4$, $^4J_{H-H} = 1.8$, imidazole-H$_5$). NH observed in d$^6$-DMSO, 3.33 ppm, br. |
| [Pt(terpy)(pyrazole)](ClO$_4$)$_2$ | 8.70–7.75 (m, 11H, terpy); 8.37 (d, 1H, $^3J_{H-H} = 2.4$, pyrazole-H$_3$); 8.33 (d, 1H, $^3J_{H-H} = 2.4$, pyrazole-H$_5$); 7.46 (s, br, 1H, NH); 7.00 (t, 1H, $^3J_{H-H} = 2.4$, pyrazole-H$_4$) |
| [Pt(terpy)(3,5-dimethylpyrazole)](ClO$_4$)$_2$ | 8.72–7.75 (m, 12H, terpy + NH); 6.53 (s, 1H, pyrazole-H$_4$); 2.62 (s, 3H, $^4J_{Pt-H} = 6$, pyrazole-Me$_3$); 2.56 (s, 3H, pyrazole-Me$_5$) |

[a] Chemical shifts for $^1$H NMR are reported by reference to TMS.




Scheme 1. Numeration of the considered five-membered N-donor heterocycles.

the spectrophotometer. The concentration of the entering group was always large enough to provide pseudo-first-order conditions. After preliminary repetitive scan experiments in the range 240–360 nm to search for isosbestic points and spectral changes, the kinetics were studied by measuring the changing absorbance at suitable wavelengths as a function of time. Pseudo first-order-rate constants ($k_{obs}/s^{-1}$) were obtained either from the gradients of plots of $\log(D_t - D_\infty)$ vs. time or from a non-linear least-squares fit of experimental data to $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_{obs}t)$ with $D_0$, $D_\infty$ and $k_{obs}$ as the parameters to be optimized ($D_0$ = absorbance after mixing the reactants, $D_\infty$ = absorbance at completion of the reaction). Rate constants were accurate to within 5%.

All the prepared complexes follow the Lambert–Beer equation in the considered concentration range and experimental conditions, so the presence of π-stacking effects [10] can be reasonably excluded.

## 3. Results and discussion

Thiazoles, oxazole, isoxazole, imidazole and pyrazoles are potentially ambidentate ligands and it is necessary to ascertain the site of binding to Pt(II) in its complexes, but there is considerable evidence to indicate bonding through nitrogen of which the following are probably the most important: (i) thiazoles and oxazoles bind to the analogous soft d$^8$ Au(III) through nitrogen [11]; (ii) thiazole ligands were found to be bonded to platinum through the nitrogen atom from data in the literature [12,13]; (iii) further proof of the Pt–N bond comes from the crystal structure of solid *trans*-[Pt(dmso)(thiazole)Cl$_2$] determined by X-ray diffraction [14]; (iv) there is a general similarity of the behaviour of these complexes with the corresponding R-py (N-containing six-membered heterocycles), that depends only upon the basicity of the nitrogen.

### 3.1. Kinetics of displacement of chloride by nitrogen donors from [Pt(terpy)Cl]$^+$

The spectrophotometric changes observed in repetitive scanning of the spectrum of the reaction mixture are characteristic of a single chemical stage, with well maintained isosbestic points. Careful examination of the spectral changes (subsequent changes have never been observed) which occur after the reagents are mixed and the close similarity of the spectra at the end of the reaction with those of authentic samples of the expected reaction products demonstrate that all the reactions that have been studied kinetically involve the displacement of coordinated chloride by the nitrogen base. The rate constants were determined in the usual way from the change

in absorbance as a function of time at a convenient wavelength within the region 300–340 nm. All the reactions were studied in the presence of a sufficient excess of nucleophile over the substrate to provide pseudo-first-order conditions and the observed rate constants, $k_{obs}$, collected in Table 3, obey to the general relationship $k_{obs} = k_1^f + k_2^f[nu]$, which is usual for nucleophilic substitution at planar four coordinate $d^8$ metal complexes [15].

Table 3
First-order rate constants, $k_{obs}$[a] for the reaction $[Pt(terpy)Cl]^+ + nu \rightarrow [Pt(terpy)(nu)]^{2+} + Cl^-$ in methanol at 25 °C

| Nucleophile | [nu] (mol dm$^{-3}$) | $10^3\,k_{obs}$ (s$^{-1}$) |
|---|---|---|
| Thiazole | 0.05 | 21.9 |
| | 0.08 | 32.7 |
| | 0.10 | 44.1 |
| | 0.12 | 54.1 |
| | 0.15 | 68.0 |
| 5-Methylthiazole | 0.02 | 12.1 |
| | 0.04 | 26.4 |
| | 0.06 | 39.1 |
| | 0.08 | 53.2 |
| | 0.10 | 63.1 |
| Imidazole | 0.003 | 21.0 |
| | 0.005 | 34.0 |
| | 0.008 | 56.8 |
| | 0.010 | 67.1 |
| | 0.015 | 101.7 |
| 4,5-Dimethylthiazole | 0.033 | 16.3 |
| | 0.066 | 28.5 |
| | 0.099 | 48.8 |
| | 0.132 | 65.1 |
| | 0.166 | 80.3 |
| 3,5-Dimethylpyrazole | 0.01 | 7.43 |
| | 0.02 | 14.7 |
| | 0.03 | 23.2 |
| | 0.04 | 29.0 |
| | 0.05 | 37.4 |
| 4-Methylthiazole | 0.05 | 17.4 |
| | 0.10 | 34.1 |
| | 0.15 | 52.9 |
| | 0.20 | 66.9 |
| | 0.25 | 89.8 |
| Oxazole | 0.15 | 27.9 |
| | 0.20 | 36.2 |
| | 0.25 | 47.2 |
| | 0.30 | 55.5 |
| | 0.35 | 65.4 |
| Isoxazole | 0.05 | 9.79 |
| | 0.10 | 21.1 |
| | 0.15 | 31.2 |
| | 0.20 | 42.3 |
| | 0.25 | 49.5 |
| Pyrazole | 0.001 | 0.48 |
| | 0.003 | 1.44 |
| | 0.006 | 2.80 |
| | 0.008 | 3.75 |
| | 0.010 | 4.92 |

[a] Errors on individual $k_{obs}$ determinations are in the ±5% range.

### 3.2. Kinetics of displacement of nitrogen donors by chloride from $[Pt(terpy)(nu)]^{2+}$

In all the reactions with an excess of chloride ion the spectrophotometric changes are characteristic of a single chemical stage, with the same isosbestic points observed for the forward reactions. The spectra at the end of the reactions coincide with those of authentic samples of the expected products at the same concentration, so that the displacement of the coordinated nitrogen donor by chloride is assured. The reactions were studied in the presence of 0.05 mol dm$^{-3}$ $CH_3SO_3H$ at constant ionic strength ($I = 0.1$ mol dm$^{-3}$, $CH_3SO_3Na$). Preliminary experiments showed that, at constant chloride concentration, the rate of reaction was independent of the concentration of the acid over the range 0.02–0.2 mol dm$^{-3}$. The acid simply serves to protonate the released nu and to prevent the reverse reaction. For the weakest bases, oxazole and isoxazole, the acid concentration is not sufficient to ensure complete protonation of the released ligand. However, because of their low basicity these species are poor ligands towards Pt(II) complexes and also in these cases a careful comparison of the spectra at the end of the reactions with the spectra of an authentic sample of $[Pt(terpy)Cl]^+$ and nu at the same concentration and acidity confirms the completion of the reactions. The observed rate constants, $k_{obs}$, collected in Table 4, obey the general relationship $k_{obs} = k_1^r + k_2^r[Cl^-]$, where $k_1^r$ and $k_2^r$ have the usual meaning, and $k_2^r$ values at $I = 0.1$ mol dm$^{-3}$ are reported in Table 5 together with the corresponding values $k_2^{0r}$ extrapolated to zero ionic strength. The extrapolation to zero ionic strength uses the Debye–Hückel relationship, $\log k_2^{0r} = \log k_2^r - 2\alpha ZaZbI^{1/2}/(1 + \beta I^{1/2})$ with $Za = +2$, $Zb = -1$, $\alpha = 1.90$ and $\beta = 1.55$ (estimated from the relative permittivity of methanol at 25 °C). [16] Preliminary experiments showed that the rate of the processes between the monocationic $[Pt(terpy)Cl]^+$ complex and the neutral nitrogen donor is not influenced by primary salt effects over the range 0.0–0.5 mol dm$^{-3}$ ionic strength, whereas that of the reverse reactions between the bis-cationic species $[Pt(terpy)\ (nu)]^{2+}$ and chloride ion depends upon the ionic strength. As a consequence the equilibrium constants, $K$, also depend upon the ionic strength and in Table 5 the values $K = k_2^f/k_2^r$ and $K^0 = k_2^f/k_2^{0r}$, determined from the ratios of the second-order rate constants for the forward and reverse reactions, are reported.

The data obtained from the reaction $[Pt(terpy)Cl]^+ + nu \rightarrow [Pt(terpy)(nu)]^{2+} + Cl^-$ are compared to the entry of pyridines and other nitrogen donors, under the same experimental conditions [3], and are reported in Fig. 1, where the values of $\log k_2^f$ are plotted against the $pK_a$ of the entering nucleophiles. As far as the unhindered thiazole, 5-methylthiazole, oxazole, isoxazole, imidazole and pyrazole are concerned, it is evident that the data fit quite nicely the linear free-energy relationships $\log k_2^f = 0.23\,pK_a + \text{constant}$ already observed for the entry of unhin-

Table 4
First-order rate constants, $k_{obs}$[a] for the reaction $[Pt(terpy)(nu)]^{2+} + Cl^- \rightarrow [Pt(terpy)Cl]^+ + nu$ in methanol at 25 °C ($I = 0.1$ mol dm$^{-3}$, $CH_3SO_3Na$)

| nu | $10^3[Cl^-]$ (mol dm$^{-3}$) | $10^3 k_{obs}$ (s$^{-1}$) |
|---|---|---|
| Thiazole | 0.25 | 8.20 |
| | 0.37 | 12.3 |
| | 0.75 | 25.7 |
| | 1.50 | 44.5 |
| 5-Methylthiazole | 0.40 | 8.41 |
| | 0.60 | 11.8 |
| | 1.00 | 16.5 |
| | 1.50 | 25.7 |
| 4,5-Dimethylthiazole | 0.20 | 0.78 |
| | 0.40 | 1.50 |
| | 0.60 | 2.26 |
| | 1.00 | 3.54 |
| 2-Aminothiazole | 0.60 | 0.12 |
| | 1.00 | 0.22 |
| | 1.50 | 0.31 |
| | 2.00 | 0.41 |
| | 2.50 | 0.49 |
| Pyrazole | 0.20 | 7.80 |
| | 0.40 | 14.9 |
| | 0.60 | 24.3 |
| | 0.80 | 31.6 |
| | 1.00 | 38.7 |
| 3,5-Dimethylpyrazole | 0.50 | 0.91 |
| | 1.00 | 1.89 |
| | 1.50 | 2.58 |
| | 2.00 | 3.72 |
| | 2.50 | 4.67 |
| 4-Methylthiazole | 0.50 | 3.03 |
| | 0.75 | 4.45 |
| | 1.25 | 6.85 |
| | 1.50 | 9.69 |
| | 2.50 | 16.1 |
| Oxazole | 0.08 | 12.2 |
| | 0.10 | 15.2 |
| | 0.12 | 19.7 |
| | 0.15 | 23.5 |
| | 0.20 | 30.9 |
| | 0.25 | 38.7 |
| Isoxazole | 0.20 | 20.3 |
| | 0.30 | 30.5 |
| | 0.40 | 41.0 |
| | 0.50 | 50.8 |
| | 0.60 | 58.7 |
| Benzothiazole | 0.20 | 9.65 |
| | 0.40 | 14.9 |
| | 0.60 | 22.8 |
| | 1.00 | 34.2 |
| | 1.50 | 50.0 |
| Imidazole | 5.0 | 0.29 |
| | 10.0 | 0.57 |
| | 30.0 | 1.71 |
| | 50.0 | 2.95 |

[a] Errors on individual $k_{obs}$ determinations are in the ±5% range.

dered pyridines on $[Pt(terpy)Cl]^+$ [3], whereas the nucleophilicity is higher ($\Delta \log k_2^f \cong 0.60$, corresponding to a difference of about 3.4 kJ mol$^{-1}$) and this fact can be reasonably ascribed to the smaller C–N–X (X = C, O, N) angle (≅108°) of the five-membered N-donors with respect to that of the pyridine (C–N–C ≅ 120°), which implies a decrease of congestion in the trigonal bipyramidal transition state. Another difference between the five-membered nucleophiles (unhindered thiazoles, oxazole, isoxazole, imidazole and pyrazoles) and pyridines in the entry reaction is the amount of steric retardation, as measured from the parameter $\Delta$[1] attributable to the presence of a methyl group in the α-position with respect to the N-donor atom. In the case of α-methylpyridines the parameter $\Delta_{f1}$ is about 1.5, corresponding to a difference of about 8.6 kJ mol$^{-1}$, and it reduces to $\Delta_{f2} \cong 0.25$ (1.4 kJ mol$^{-1}$) for the entry of 4-methylthiazole, 4,5-dimethylthiazole and 3,5-dimethylpyrazole on the same complex.

The amount of steric retardation is related to the free rotation of the ligand molecule around the Pt–N bond, which leads to steric interference with the pyridine rings of the terpy ligand placed in the axial position in the trigonal bipyramidal transition state. For this reason, the differences in reactivity can be explained by considering the different structures of the pyridines compared to that of the five-membered N-donors (Scheme 2), which leads to a decrease in steric congestion in the latter compounds if compared to the former.

As far as the reverse reaction is concerned, the replacement of the N-ligands by $Cl^-$, the differences between the five-membered heterocycles and the pyridines groups are quite evident. In the replacement reactions of the N-ligand from the bis-cationic Pt-terpy substrate by chloride, the six five-membered N-donors are significantly less labile than the unhindered pyridines (Fig. 2).

The dependence of the lability of the two kinds of ligands upon basicity is almost the same and the data fit nicely the free-energy relationship $\log k_2^r = -0.51\ pK_a$ + constant already reported [3] for the displacement of unhindered pyridines, and the decrease in lability corresponds to a difference of about 3 kJ mol$^{-1}$ between the free energy of activation of the two reacting systems. The lability of the five-membered N-donor heterocycles is considerably lower than that of pyridines, strongly suggesting that, in addition to possible but unlikely solvatation effects, the Pt–N bond in the case of five-membered N-donors may be reinforced by π bonding. It seems reasonable to conclude that the π system of five-membered N-donors can interact in the ground state with the filled d orbitals of Pt(II) better than pyridines. The fact that the thiazoles are weaker σ donors but fairly better π acceptors than pyridines once coordinated to Pt(II) has been pointed out in a work concerning hydrogen isotope exchange in Pt(II)-thiazole systems [18]. Also in the present study, for the pyridines system, the relatively large dependence of the

[1] $\Delta$ can be regarded as the steric effect due to the introduction of a methyl group *ortho* to the nitrogen in the entering nucleophiles without any interference from the basicity change that might arise from the presence of the substituent.

Table 5
Second-order rate constants[a] and equilibrium constants for the reaction $[Pt(terpy)Cl]^+ + nu \underset{k_1^r+k_2^r[Cl^-]}{\overset{k_1^f+k_2^f[nu]}{\rightleftharpoons}} [Pt(terpy)nu]^{2+} + Cl^-$

| Nucleophile | $10^2k_2^f$ (dm$^3$ mol s$^{-1}$) | $10^2k_2^r$ (dm$^3$ mol s$^{-1}$) | $10^2k_2^{0r}$ (dm$^3$ mol s$^{-1}$) | $10^2K(k_2^f/k_2^r)$ | $10^2K^0(k_2^f/k_2^r)$ | p$K_a$ of nuH$^+$ |
|---|---|---|---|---|---|---|
| Thiazole | 47 ± 2 | 2800 ± 200 | 114800 | 1.6 ± 0.2 | 0.041 | 2.55 |
| 4-Methylthiazole | 36 ± 1 | 660 ± 40 | 27060 | 5.5 ± 0.9 | 0.133 | 3.26 |
| 4,5-Dimethylthiazole | 49 ± 1 | 345 ± 9 | 14145 | 14.2 ± 0.6 | 0.346 | 3.73 |
| Imidazole | 670 ± 10 | 5.9 ± 0.9 | 241.9 | 11300 ± 300 | 2.769 | 7.65 |
| Benzothiazole | | 3120 ± 60 | 127920 | | | 1.2 |
| Oxazole | 18.8 ± 0.4 | 15400 ± 400 | 631400 | 0.122 ± 0.006 | 0.003 | 0.8 |
| 2-Aminothiazole | | 19.5 ± 0.7 | 799.5 | | | 5.36 |
| 5-Methylthiazole | 64 ± 2 | 1500 ± 100 | 61500 | 4.3 ± 0.4 | 0.104 | 3.12 |
| Pyrazole | 48 ± 1 | 3900 ± 100 | 159900 | 1.23 ± 0.06 | 0.030 | 2.48 |
| 3,5-Dimethylpyrazole | 74 ± 2 | 150 ± 20 | 6150 | 49 ± 8 | 1.203 | 4.38 |
| Isoxazole | 20.1 ± 0.1 | 9700 ± 300 | 397700 | 0.207 ± 0.007 | 0.005 | 1.30 |

p$K_a$ values were taken from Ref. [17].
[a] Determined by weighted linear regression of $k_{obs}$ values vs. nucleophile concentration.

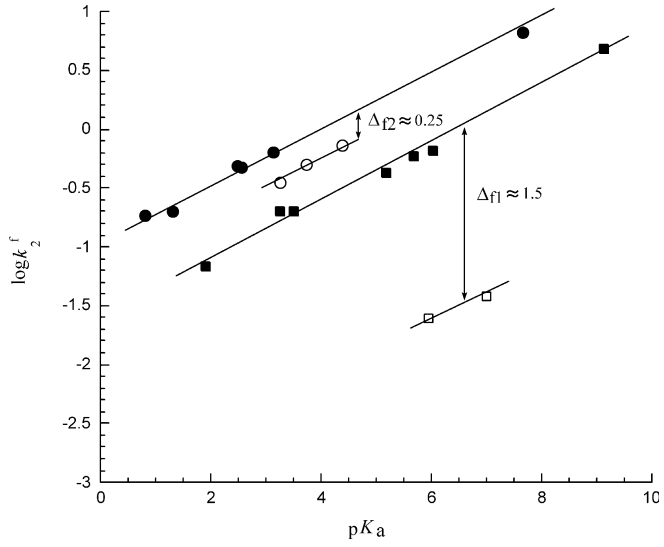



Fig. 1. $\log k_2^f$ for the reaction $[Pt(terpy)Cl]^+ + nu \rightarrow [Pt(terpy)(nu)]^{2+} + Cl^-$ plotted against p$K_a$ of nuH$^+$: ●, oxazole, isoxazole, pyrazole, thiazole, 5-methylthiazole, imidazole; ○, 4-methylthiazole, 4,5-dimethythiazole, 3,5-dimethylpyrazole; ■, 4-cyanopyridine, 4-acetylpyridine, methylisonicotinate, pyridine, 4-methylpyridine, 3-methylpyridine, 4-aminopyridine; □, 2-methylpyridine, 2,4-dimethylpyridine; data for all the pyridines were taken from Ref. [3].

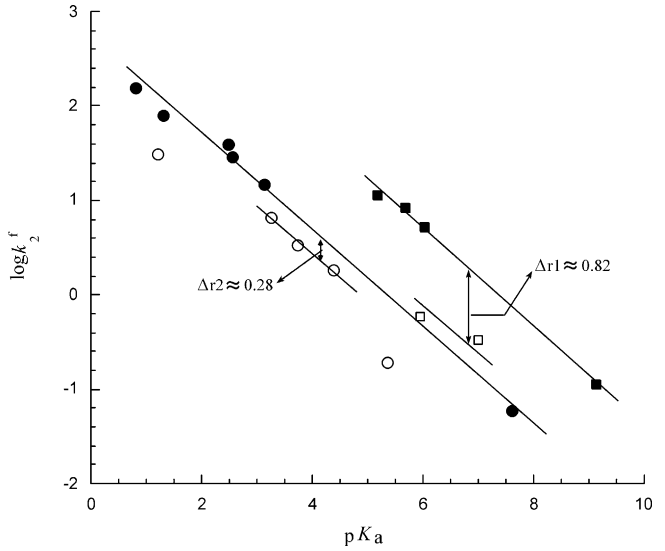
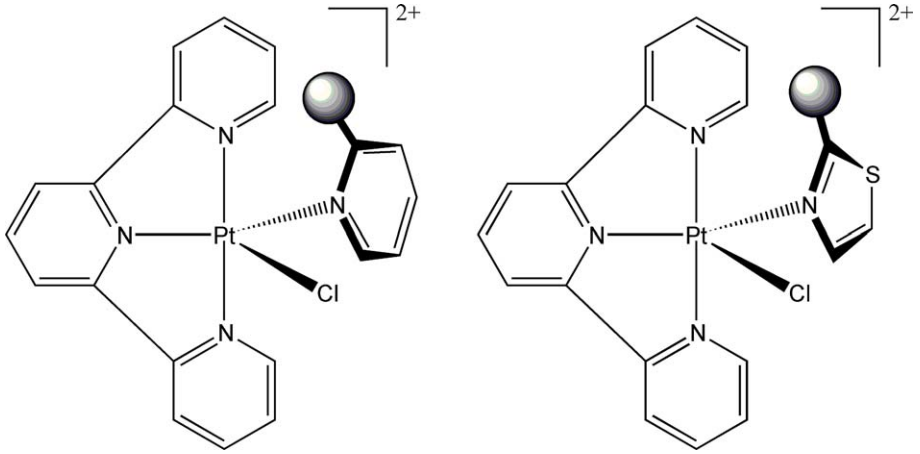



Fig. 2. $\log k_2^r$ for the reaction $[Pt(terpy)(nu)]^{2+} + Cl^- \rightarrow [Pt(terpy)Cl]^+ + nu$ plotted against p$K_a$ of nuH$^+$: ●, oxazole, isoxazole, pyrazole, thiazole, 5-methylthiazole, imidazole; ○, 4-methylthiazole, 4,5-dimethythiazole, 3,5-dimethylpyrazole; ■, pyridine, 4-methylpyridine, 3-methylpyridine, 4-aminopyridine; □, 2-methylpyridine, 2,4-dimethylpyridine; data for all the pyridines were taken from Ref. [3].




Scheme 2. Steric congestion in the trigonal bipyramidal transition state for substituted pyridines and thiazoles.

substitution lability upon ligand basicity suggests that the formation of the transition state requires a considerable change in the Pt–N bond, confirming therefore the observation already reported [1,4] that the transition state can be described as a structure containing a well formed Pt–Cl bond and a weak Pt–N bond. As far as the lability of hindered five-membered N-donors (4-methylthiazole, 4,5-dimethylthiazole and 3,5-dimethypyrazole) in the reverse reactions of process (1) is concerned, a lower (as expected, see above) steric effect for five-membered N-donors ($\Delta \cong 0.28$, 1.4 kJ mol$^{-1}$) than for pyridines ($\Delta \cong 0.82$, 4.6 kJ mol$^{-1}$) has been observed (Fig. 2). Not only α-methyl-substituted five-membered heterocycles, but also other ligands such as 2-aminothiazole and benzothiazole were considered. For these substrates the $\Delta$ value is higher (0.70, 3.9 kJ mol$^{-1}$) than that measured for 4-methylthiazole, 4,5-dimethylthiazole and 3,5-dimethylpyrazole. This difference is due to the greater congestion on the metal centre caused by the $NH_2$- and benzo-substituents, which disfavours the platinum–chloride bond formation. The ratio between the second-order rate constants for the forward and reverse reactions gives the corresponding equilibrium constants for the systems:

$$[Pt(terpy)Cl]^+ + nu \rightleftharpoons [Pt(terpy)(nu)]^{2+} + Cl^-$$

and the actual values of $K$ at $I = 0.1$ mol dm$^{-3}$ and $K^0$ at zero ionic strength are reported in Table 5. The plot of $\log K^0$ versus $pK_a$ (Fig. 3) is linear for the group of five-membered N-donors formed by thiazole, 5-methylthiazole, oxazole, isoxazole, imidazole and pyrazole, and the free energy relationship $\log K^0 = (0.74)pK_a + \text{constant}$ can be derived.

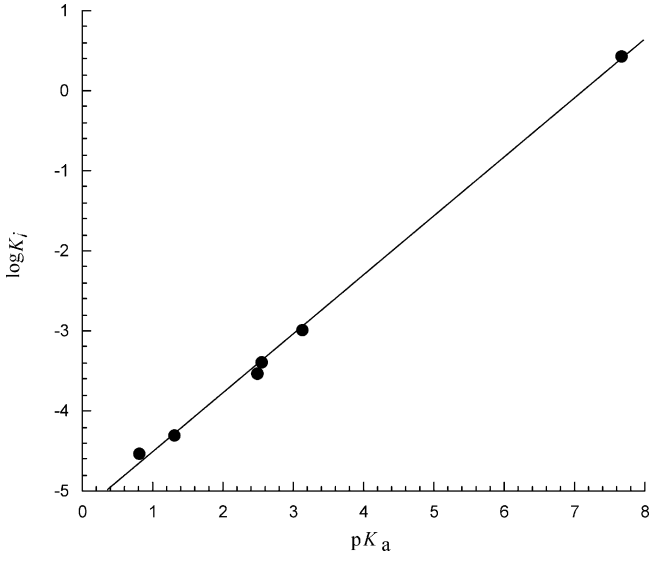



Fig. 3. $\log K^0$ for the reaction $[Pt(terpy)Cl]^+ + nu \rightleftharpoons [Pt(terpy)(nu)]^{2+} + Cl^-$ plotted against $pK_a$ of $nuH^+$: ●, oxazole, isoxazole, pyrazole, thiazole, 5-methylthiazole, imidazole.

The dependence of the stability of the complexes upon the basicity of the ligands is the same as that measured for pyridines under the same experimental conditions [3]. However, the values of the equilibrium constants are higher than those found in the previous case. Such a difference may reflect a greater tendency of five-membered N-donors, in comparison with pyridines, to give π back-donation from the filled orbitals of the metal to the antibonding orbitals of the ligand, leading to a relative stabilization of the ground state of the products.

## Acknowledgements

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