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Interaction of nitrogen bases with some platinum(II) and palladium(II) complexes—usual and unusual features

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Contents

Abstract

This short review describes the kinetic interaction of several platinum(II) and palladium(II) complexes with various nitrogen bases. The reactions have been categorized with the type of metal complexes. The reaction patterns of amine and ammine, pyridine-2-carboxylate, pyridine-2,6-dicarboxylate and pyridoxine complexes with the above metal ions have been discussed. Some unusual features in the above reactions have been noted.

Keywords: Platinum(II) and palladium(II) complexes; Nitrogen base interaction; Kinetic studies

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1. Introduction

The square-planar complexes of platinum(II) and palladium(II) are of increasing importance since the discovery of the anti-tumor property of *cis*-dichlorodiammine-platinum(II) [1]. Today's research on such complexes centres around: (i) synthesis of model compounds which would mimic the metal ion interaction with proteins in living systems; (ii) studies related to observing the effect of metal ions on the conformation and physico-chemical properties of a coordinated moiety, e.g. amino acid or peptide and (iii) designing of new types of anti-cancer drugs which would be effectively transported through cell membranes to the malignant cells. Apart from these, kinetic studies on the interaction of various platinum(II) and palladium(II) complexes with nucleophiles may often lead to fascinating features related to solution chemistry. The present lecture touches upon some observations made recently.

2. General aspects of nucleophilic interaction

Detailed kinetic studies of nucleophilic interaction with platinum(II) and palladium(II) complexes support an associative(A) mechanism [2]. This has been very nicely narrated by Basolo in a recent review [3]:

> "A massive amount of kinetic studies now support the S_N2 mechanism, so much so that when Romeo and coworkers [4,5] discovered S_N1 reactions of platinum(II) complexes, the referees delayed publication because of the strong belief that all platinum(II) substitutions are S_N2."

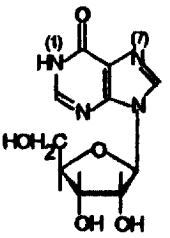
(The reference number has been changed for convenience).

The involvement of a solvolytic path (k_1) along with the direct substitution path (k_2) is often encountered in such reactions, and the usual rate expression assumes the form

$$k_{obs} = k_1 + k_2[B]$$ where B is a nucleophile.

3. Interaction of amine and ammine complexes of platinum(II) and palladium(II) with nitrogen bases

There has been considerable interest in the reactions of platinum(II) complexes with purine nucleosides and related compounds in the past decade [6]. The complexation of $[Pt(dien)H_2O]^{2+}$ (dien = diethylenetriamine) with the model nucleobases, inosine (**1**) and 1-methylinosine (**2**) takes place via the aqua cation in the range pH 4.2–8.4 [7].



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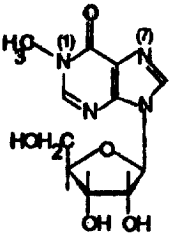

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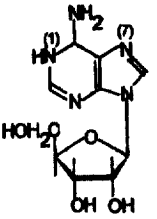
The corresponding deprotonated species $[Pt(dien)OH]^+$ ion is considered to be inert towards substitution. The aqua-Pt(dien) binds exclusively to N(7) in both nucleosides. With an increase in pH > 6, the N(1) site becomes an additional coordination site owing to the deprotonation of N(1)H. In any case the N(7) site is favored over N(1) kinetically, though the intrinsic formation reactions of the N(1), N(7) bound diplatinum complex via N(1)- and N(7)-bound 1:1 complexes are kinetically equivalent. A very recent study [8], however, shows that prolonged treatment of aquated Pt^{II}(dien) with an excess of adenosine (3) at ca. 85°C in aqueous solution leads to a considerable increase in the proportion of N(1)-bound species at the expense of the N(7)-isomer.



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It has been possible to isolate both the isomers chromatographically and characterize through ^1H-,^{13}C- and ^{195}Pt-NMR spectroscopy showing the existence of two different environments of Pt^{II}. The *trans*-$[PtCl(NH_3)_2(H_2O)]^+$ behaves like the monofunctional $[Pt(dien)(H_2O)]^{2+}$ in the range pH 2.8–8.4 [9] due to the greater *trans*-effect exerted by Cl^- over H_2O. Moreover, the magnitudes of the corresponding rate parameters roughly match each other suggesting that the *trans*-effect of Cl^- is similar to that of the –NH group in the tetradentate dien ligand. The relative reactivity of *trans*-$[PtCl_2(NH_3)_2]$, *trans*-$[PtCl(NH_3)_2(H_2O)]^+$ and *trans*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ towards inosine is ca. 1:200:10 in keeping with the *trans*-effect order, $Cl > NH_3 \approx$ ino-N(7)$> H_2O$.

Among the *cis*-diammine complexes the majority of kinetic studies pertain to the complexation features of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ [10]. The complexation of guanosine 5′-monophosphate with *cis*-$[PtCl_2(NH_3)_2]$ or its ethylenediamine analogue is believed to occur via the dichloro compound and the corresponding monoaqua species at pH 6.5 but not via the diaqua species [11]. With adenosine, on the other hand, *cis*-$[PtCl(NH_3)_2(H_2O)]^+$ has been reported to react 15 times faster than the *cis*-$[PtCl_2(NH_3)_2]$ at pH 3 [12]. A HPLC study on the kinetics and

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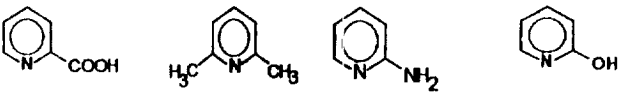
mechanism of interaction of *cis*-$[PtCl_2(NH_3)_2]$ and its hydrolytic product with inosine in slightly acidic aqueous medium (pH 3.5-4.0) [13] shows the first hydrolytic product of cisplatin to be the active intermediate. The direct substitution of the chloro ligand as well as the role of the second hydrolytic product seem to be relatively insignificant.

A recent study [14] of the kinetics of interaction of $[Pt(dien)Br]^+$ with some nitrogen heterocycles (**4–7**) in aqueous medium reveals the existence of a biphasic interaction apparent from the first-order semilog plots of absorbance-time or conductance-time data. Rate measurements under pseudo-first-order conditions with the nitrogen bases present in 10–100 times excess of the $[Pt(dien)Br^+]$ by both methods show identical results. Rimm et al. [15] in an earlier study on the kinetics of interaction of $[Pt(dien)Br]^+$ with a large number of pyridine bases of the type (**8–11**) followed conductometrically encountered initial deviations from the first-order rate plots at low pyridine concentrations.



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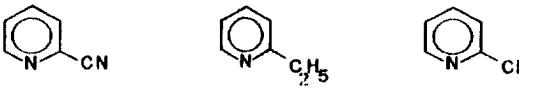
This was attributed to the addition of an insufficient amount of ligand to produce pseudo-first-order kinetics, and the rate constants were evaluated by ignoring the initial points. The rates of substitution of bromide were found to be governed primarily by steric properties of the entering group. There was no general relationship between this rate and the basicity of the pyridine derivatives. At about the same time Chan and Wong [16] observed such a deviation even at high base concentrations in analogous reactions of $[Pt(dien)Br]^+$ with 2-substituted pyridines of the type (**12–14**). No proper explanation of the initial deviations from the usual first-order plots has been put forward in either case.



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The interaction of 'pseudo-bases' of the incoming nucleophiles in the reaction medium as suggested by Gillard et al. [17–19] is of no significance here. We noted that this type of deviation in the pseudo-first-order plots is noted with aged solutions of $[Pt(dien)Br]^+$ only. The aquated Pt–dien reacts faster than the bromo analogue causing an apparent deviation in rate plots. Under comparable conditions the reactivity of the aqua complex is ca. 20 times higher than that of the bromo analogue. Our observation is comparable to that by Bose et al. [20] who have

shown that the monoaqua analogue of *cis*-$[Pt(NH_3)_2Cl_2]$ reacts at a faster rate than the dichloro complex in its reaction with cysteine, causing deviation in first-order rate plots. The analysis of the bulk reaction involving the $[Pt(dien)Br]^+$ yields the usual solvolytic path and the direct nucleophilic attack. Only mild steric, inductive or other effects are noted for these aza bases. The adducts formed in each case have been characterized by elemental analysis, IR and ^{1}H-NMR measurements.

The corresponding reactions of $[Pd(dien)Br]^+$ with imidazole (**3**) and benzimidazole (**4**) followed conductometrically are ca. 10^5–10^6 times faster. This is compatible to earlier observation whereby $[Pd(dien)SCN]^+$ reacts ca. 7×10^5 times faster than the Pt(II) analogue [21]. It has been proposed [22] that the kinetics of interaction of the $[Pd(dien)]^{2+}$ center with nucleobases and nucleosides deviates markedly from the normal square-planar substitution behavior in that the usually fast anation step following the rate-determining solvolysis is slowed down to such an extent by the nitrogen donors that it becomes rate-determining under all conditions.

Kinetic studies on the forward and reverse reactions of the process $[Pt(terpy)Cl]^+ + amine \Leftrightarrow [Pt(terpy)(amine)]^{2+} + Cl^-$ (terpy = 2,2′:6′,2″-terpyridine; amine = NH_3 and a number of pyridine derivatives having a wide range of basicity) have been carried out in methanolic solution [23]. The specific second-order rate constants, k_2^f (25°C) follow the LFER, $\log k_2^f = \alpha pK_a + \text{constant}$ with $\alpha = 0.24$ for the entry of the isosteric pyridine, 4-cyanopyridine, and methylisonicotinate etc. The reactivity of NH_3 is slightly less compared to the above pyridines, and this has been attributed to the small differences in solvation of the ligands and/or to a small contribution of π-interactions for the latter bases.

In the same way, the LFER plot for the dependence of the reactivity upon the basicity of leaving N-base ligands leads to a value of $\alpha = -0.53$ for the complexes with the unhindered pyridines, e.g. 3-methylpyridine, 4-methylpyridine and 4-aminopyridine. The ability of the chloro-complex to discriminate among the nucleophiles, as well as the sensitivity of the rate of chloro entry on the nature of the displaced N-base, and the steric factors for both the forward and reverse reactions have been compared with the data for a number of other platinum(II) complexes [24–28]. The intimate mechanism evolved from such studies points to a transition state for all these substitutions in which the Pt–N bond is only partially formed in the rate-determining transition state, whereas the Pt–Cl bond is practically formed to the same extent in the ground and transition states. The equilibrium constants for these reactions have been evaluated from the ratio of the forward and reverse rate constants.

4. Interaction of pyridinecarboxylate complexes of platinum(II) with nitrogen bases

Studies related to the interaction of $[PtCl_4]^{2-}$ [29] and mono-anionic complexes of the type $[PtLCl_3]^-$ (L = $(CH_3)_2SO$, $(CH_3)_2S$, $(C_2H_5)_2S$, PR_3, $P(OMe)_3$, $As(C_2H_5)_3$ [30–34] with amines and heterocyclic bases are reported in the literature, but little is known about the nitrogen base interaction with pyridinecarboxylate complexes of platinum(II). In the reactions of $[Pt(pic)(L)(Y)]^-$ (where H_2pic = pyridine-2-car-

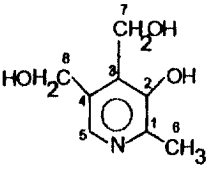
boxylic acid; L = Cl, NO_2; Y = Cl) with the Lewis bases e.g. N_3^-, NCS^- and NO_2^-, kinetic data show [35] that these are much more reactive than their n^0_{Pt} values. The addition of a hydroxide ion does not affect the rate of reaction with azide and so the anomaly cannot be ascribed to the catalysis by HN_3 which would be suppressed by this treatment or to attack on the carbonyl carbon which the hydroxide could do much more effectively. [Pt(dipic)(H_2O)] (H_2dipic = pyridine-2,6-dicarboxylic acid) is claimed [36] to be the first structurally characterized example of a mononuclear Pt^{II} complex with an N_1O_3 donor atom set. The kinetics of anation reactions of this complex with an excess of aza-bases e.g. imidazole and benzimidazole in DMF medium [37] assumes significance in view of the fact that a tridentate 'dipic' ligand (*N,O,O*-coordination) transforms to a bidentate one (*N,O*-coordination) allowing the entry of a second molecule of the aza-base in the course of the reaction. This is reflected in the computer-fit analysis of the kinetic data in terms of a two exponential process. The ring opening reactions of mixed nitrogen–oxygen chelates of platinum(II) complexes have been examined earlier [38]. The facile cleavage of one of the carboxylate groups from the platinum(II) centre is likely to be a consequence of the steric strain as well as the more ionic nature of the Pt–O bond than that of the Pt–Cl bond. The bidentate (unsymmetrical) coordination of the dipic ligand is confirmed from IR and NMR results of the bis-substituted product complexes. The similar type of partial ring-opening in the reactions of [Pt(dipic)Cl]$^-$ with methionine and its derivatives has been confirmed by Zhou and Kostic et al. [39] from NMR studies. The stoichiometric (1:1) reaction of the aza bases with [Pt(dipic)(H_2O)] always produces the mono-substituted species as a thermodynamically stable product. Each phase of the biphasic substitution reaction has been ascertained by preparing the intermediate mono-substituted aza-base product, and further examining its reaction with the corresponding base in excess. These rate constants are analogous to the corresponding values of the second phase of the biphasic reactions. A squared-dependence of rate on [pyrazole] is noted under the identical reaction conditions. A probable mechanistic path may be invoked as the formation of a monosubstituted complex from the aqua substrate as an intermediate which can further take up another pyrazole molecule by the rupture of a Pt–O bond with a comparable rate. Earlier studies by Cattalini et al. [40] have also indicated biphasic reaction traces in the interaction of [Pt(dipic)Cl]$^-$ with sulfite and thiocyanate, but no detailed kinetic analysis has been attempted. It merely considers the faster reaction step corresponding to the nucleophilic substitution of the monofunctional Pt^{II}-substrate.

The reactions of [Pt(dipic)(NO_2)]$^-$ with imidazole and benzimidazole show apparent triphasic absorbance changes with time. The initial rapid phase may be attributed to a faster pseudo-base path in addition to the normal base component for the formation of the mono-substituted complex; the ring-cleavage process also corresponds to an absorbance change. A computer-fit biphasic analysis of data indicates that the removal of the $-NO_2$ group through the pseudo-base occurs at the fastest rate whereas the normal base reacts at the slowest rate. The ring-opening process involving the introduction of a further aza-base, on the other hand, occurs at the intermediate rate. The pseudo-base formation may be conceived through the

abstraction of an imino-hydrogen atom from the aza-base in DMF medium (formal pH 10–12). The formation of a pseudo-base involving amine type of ligands, e.g. ethylenediammine in pure DMF medium has been established earlier [41] through the interaction of DMF with amine proton via the formation of a strong hydrogen bond. The dominant role of the negatively charged $[Pt(dipic)(NO_2)]^-$ seems to be important since no such phenomenon is noted for other neutral Pt(II) substrates. The triphasic absorbance change during the reaction of $[Pt(dipic)Cl]^-$ with excess nitrite observed by Cattalini et al. [40] considers the first-phase as the removal of Cl^- by nitrite, followed by the further introduction of another NO_2^- to the mono-substituted complex. The third phase has been ignored owing to its sluggish nature and small contribution to the overall absorbance change.

5. Interaction of pyridoxine complex of palladium(II) with nitrogen bases

The compounds comprising the vitamin B_6 complex, including pyridoxal, pyridoxamine and pyridoxine, display a variety of coordination sites with different charges and hard–soft character of metals, offering a rich coordination chemistry. The structures of *cis*- and *trans*-$[PdCl_2(PN)_2]$ (PN = pyridoxine) (**15**) has been deduced from single crystal X-ray and IR spectroscopic studies which show that the pyridoxine ligands are coordinated through the pyridine nitrogen [42].



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The ^{13}C-NMR spectrum of *trans*-$[PdCl_2(PN)_2]$ displays two resonances of almost equal intensity for C(1), C(3), C(5) and C(6). No such behaviour is observed for the *cis*-$[PdCl_2(PN)_2]$. The possibility of the DMSO solvent displacing the PN ligand which may render the observed peaks is ruled out owing to: (i) the peaks for solutions of the complex are different from those for a solution of the ligand alone in DMSO; (ii) there is no change in the spectral pattern (peak heights and peak positions) with respect to time. The doublets have been assigned to the presence of two rotamers of the *trans*-$[PdCl_2(PN)_2]$, one having the PN ligand disposed in a way that the C(6) methyl groups lie on opposite sides of the $[PdCl_2(PN)_2]$ plane, and the other has one of the ligands rotated through 180° about the Pd–N bond axis, so that the methyl groups fall on the same side of the plane.

Kinetics of the interaction of *trans*-$[PdCl_2(PN)_2]$ with imidazole, benzimidazole and pyrazole have been followed in DMSO at 30°C spectrophotometrically [43]. The salient features observed in the spectral scanning in the region 250–350 nm on mixing solutions of the complex (2×10^{-4} M) with the aza bases (2×10^{-3} M) are as follows.

(i) There is a rapid decrease in absorbance of ca. 0.7 at the λ_{max} (= 280 nm) in comparison to the parent complex within a time-period ca. 10 s with the imidazole and pyrazole systems; residual absorbance of benzimidazole in this range obviates the observation of sudden decrease in absorbance.

(ii) Repetitive spectral scanning at intervals of 1 min shows a downward trend in absorbance in the reaction of all the aza bases, and after a certain period of time (ca. 7 min), it starts to increase slightly, finally attaining a constant value. The kinetic course of the absorbance change as in (i) has been followed by stopped-flow spectrophotometry, and that of (ii) by conventional UV–vis spectrophotometry. Each of these shows biphasic reaction traces. The faster phases are due to the replacement of the two chloride ligands and the slower phases to the replacement of two PN groups.

In repeated attempts to isolate the products under experimental conditions, i.e. reacting an excess of the aza bases with respect to the Pd^{II}-complex, the expected $[PdX_4]Cl_2$ (where X = imidazole, benzimidazole and pyrazole) was not obtained in the pure state. Rather, analytical results correspond closely to $[PdX_3Cl]Cl$.

Based on the results of the product analysis along with the biphasic nature of the kinetic curves, a possible sequence of reactions can be framed:

$$[PdCl_2(PN)_2] + X \Leftrightarrow [PdXCl(PN)_2]^+ + Cl^-$$

$$[PdXCl(PN)_2]^+ + X \Leftrightarrow [PdX_2(PN)_2]^{2+} + Cl^-$$

$$[PdX_2(PN)_2]^{2+} + X \Leftrightarrow [PdX_3(PN)]^{2+} + PN$$

$$[PdX_3(PN)]^{2+} + X \Leftrightarrow [PdX_4]^{2+} + PN$$

The observed rate constants (k_{obs}) from the biphasic reaction traces for the replacement of chloride and PN ligands can be fitted linearly to the concentration of the azole bases as

$$k_{obs(a)} = k_{1(a)} + k_{2(a)}[X]$$

$$k_{obs(b)} = k_{1(b)} + k_{2(b)}[X]$$

In order to confirm such a multistep reaction behavior pure $[Pd(imidazole)_4]Cl_2$ (colorless powder) and *trans*-$Pd(imidazole)_2Cl_2$ (yellow crystals) were synthesized following literature methods [44].

A spectral scanning of a mixture of *trans*-$Pd(imz)_2Cl_2$ (10^{-4} M) and imidazole (10^{-3} M) shows a similar type of drop in absorbance within ca. 10 s of mixing and then a slight increase in absorbance (λ_{max}, 260 nm) leading to an equilibration. The spectrum of a DMSO solution of $[Pd(imz)_4]Cl_2$ (10^{-4} M) with an excess of imidazole (10^{-3} M) is quite identical to that of the above equilibrated solution. This observation leads one to believe that, though $[Pd(imz)_4]Cl_2$ is formed in solution by the replacement of Cl^- and PN ligands during kinetic study, it is not stable in the medium and an equilibrated mixture prevails, and that is why the expected $[Pd(imz)_4]Cl_2$ cannot be obtained in the pure state in the attempt to synthesise the same. The following equilibrium may be of importance here:

$$[Pd(imz)_4]Cl_2 \Leftrightarrow [Pd(imz)_3Cl]Cl + imz$$

The kinetic results for the interaction of benzimidazole with the palladium(II) complex yields limiting rates at higher concentrations of the N-base (0.05–0.1 M) during the (slower) reaction steps of the removal of PN ligands. A pre-equilibrium association between the Pd(II)-complex and the benzimidazole base is apparent. Since both species are uncharged, there is no chance of ion-pair formation. Hydrogen-bond interaction between the NH– group of benzimidazole and the OH– group of the pyridoxine ligand of the substrate may be of significance for the formation of the associated species. Stacking interaction involving the Π-cloud of the aromatic ring of benzimidazole moiety would facilitate such a process.

6. Conclusions

Detailed discussions are available on the nucleophilic base interactions with platinum(II) and palladium(II) complexes. The material of this review has been presented from the standpoint of some usual and unusual features encountered in such reactivity studies. These are likely to become more amenable to kinetic and spectroscopic scrutiny.

Acknowledgements

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