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Supplementary Material Available: Tables of data collection parameters, atomic parameters, anisotropic thermal parameters, hydrogen atom parameters, and interatomic distances and angles for 2 and 3 (14 pages); tables of structure factors for 2 and 3 (21 pages). Ordering information is given on any current masthead page.

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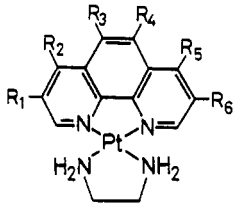
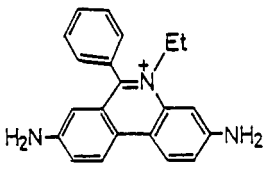
Thermodynamic Nucleic Base Specificity in Nucleotide–Metallointercalator Association. Structure–Stability Relationship Showing Significant Contribution of the Amino Group to Aromatic Ring Stacking

Intercalation of planar compounds into base pairs of DNA greatly influences the properties of DNA and is thought to be the first step in mutagenesis.[1] Platinum(II) and other metal complexes with heteroaromatic rings (L) such as bpy and phen interact with DNA and nucleotides by stacking interactions with the base pairs.[2,3] The positive charge of the Pt(II) complexes probably contribute to intercalation through the initial electrostatic bonding with the phosphate oxygens of DNA.[4] Our previous circular dichroism (CD) and ^{1}H NMR spectral studies on the intercalation of the platinum(II) intercalators Pt(L)(en) (L = bpy, phen,



Pt(L)(en)



ethidium

L = phen ($R_1=R_2=R_3=R_4=R_5=R_6=H$)
Me_2phen ($R_1=R_2=R_5=R_6=H$, $R_3=R_4=CH_3$)
Me_4phen ($R_1=R_2=R_5=R_6=CH_3$, $R_3=R_4=H$)

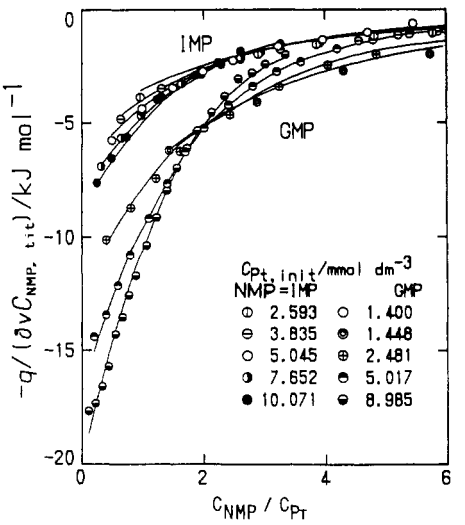


Figure 1. Calorimetric titration curves for Pt(phen)(en)–GMP and –IMP systems at pH 7–8 and 25 °C (I = 0.1 M (NaCl)). Key: q, heat liberated per unit volume of titer; C_{NMP}, concentration of NMP; C_{Pt}, concentration of Pt(L)(en).

Table I. Stability Constants, log β_1, and Thermodynamic Quantities, $\Delta H_1°$ and $\Delta S_1°$, for 1:1 Intercalator–NMP Adduct Formation at 25 °C and pH 7–8 (I = 0.1 or 0.2 M (NaCl))[a]

intercalator	NMP	I, M	log β_1[c]	$\Delta H_1°$/kJ mol^{-1}	$\Delta S_1°$/J mol^{-1} K^{-1}
Pt(phen)(en)	IMP	0.1	2.34 (0.08)	−11.9 (0.9)	5
	GMP[b]	0.1	2.49 (0.03)	−26.2 (0.8)	−40
	AMP[b]	0.1	2.51 (0.03)	−25.6 (0.8)	−38
	CMP	0.1	2.17 (0.08)	−6.5 (0.5)	20
ethidium	IMP	0.2	1.86 (0.14)	−4.0 (0.5)	22
	GMP	0.2	2.01 (0.04)	−9.1 (0.3)	8
	AMP	0.2	1.92 (0.13)	−9.3 (1.1)	6

[a] Values in parentheses denote estimated standard deviations. [b] Taken from ref 8. [c] Units of β_1 are mol^{-1} dm^3.

Me_4phen) with several mononucleotides (NMP) as fundamental constituents of nucleic acids have shown that the intercalators have an intrinsic tendency to stack with nucleotides and nucleosides in dilute aqueous solution.[5] In addition to the structural studies on related metallointercalator–nucleotide adducts[6] the X-ray crystal structure analysis of an adduct [Pt(bpy)(en)]·AMP·10H_2O also revealed the stacking between bpy and the adenine ring of AMP,[7] supporting the conclusion from the spectra. As an extension of these studies[5,7,8] we investigated adduct formation between Pt(L)(en) and NMP containing purine and pyrimidine bases with or without an amino group. An important effect of the nucleic base amino group, which is involved in the hydrogen bonds between base pairs in DNA, is that it alters the electron density of the base,[9] and this is potentially related to the base specificity of intercalators and other reagents that have affinity for nucleic acids. We here report the systematic thermodynamic characterization of Pt(L)(en)–NMP adduct formation and the NMR spectral evidence that the amino group attached to the nucleic bases makes a substantial contribution to the stacking

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interaction with the platinum intercalators as well as with ethidium bromide, a well established DNA intercalator.[10] The $\Delta H_1°$ values for the intercalator–NMP interactions are more favorable for NMP = AMP and GMP than for CMP, UMP, and IMP, of which the latter two are devoid of the amino group.

The calorimetric titration curves for Pt(phen)(en)–GMP and –IMP demonstrated that there is a definite difference between IMP and AMP or GMP and between CMP and UMP in the heat liberated upon adduct formation (Figure 1).[11] The equilibrium constants, β_n, for the following equilibrium were determined by nonlinear least-squares curve fitting[11] by considering 1:1 and 1:2 adducts (n = 1 and 2, L = phen, and charges are omitted for simplicity):

$$\mathrm{Pt(L)(en)} + n\mathrm{NMP} \overset{\beta_n}{\rightleftharpoons} \mathrm{Pt(L)(en)}\cdots(\mathrm{NMP})_n$$

$$\beta_n = \frac{[\mathrm{Pt(L)(en)}\cdots(\mathrm{NMP})_n]}{[\mathrm{Pt(L)(en)}][\mathrm{NMP}]^n}$$

The log β_1 values and thermodynamic parameters obtained are summarized in Table I. The $-\Delta H_1°$ values for AMP and GMP,[8] 25.6 and 26.2 kJ mol^{-1}, respectively, are much larger than expected for hydrophobic interactions (5–10 kJ mol^{-1})[12] and are interpreted as due to cooperative effects of the electrostatic and stacking interactions and contribution of the charge-transfer interactions between coordinated phen and the purine rings[13,14] in addition to the dipole–dipole contribution. Most interestingly the $-\Delta H_1°$ value for IMP, which lacks the amino group, is less than half of the values for GMP and AMP, and a similar trend is seen for the ethidium–NMP adducts (Table I), suggesting that such a structural dependence of $\Delta H_1°$ values holds true for other intercalator–nucleotide interactions.[15] Adduct formation with the pyrimidine nucleotides gave a small $-\Delta H_1°$ value for CMP, which was compensated by a large $\Delta S_1°$ value to make the adduct stability comparable with that of AMP and GMP. No liberation of heat was observed for UMP, which is devoid of the amino group, and it was not possible to determine the stability constants by the calorimetric method. Table I shows that the adducts with a large $-\Delta H_1°$ value have a large negative $\Delta S_1°$ value (–38 to ~–40 J mol^{-1} K^{-1}), which makes a negative contribution to the adduct stabilization by stacking in Pt(phen)(en)–AMP or –GMP. For Pt(phen)(en)–IMP and –CMP and the adducts with ethidium bromide which exhibit small $-\Delta H_1°$ values, the entropy terms are positive. Such thermodynamic behavior of the adducts may be explained by the solvophobic force[16] involving both enthalpy and entropy effects.

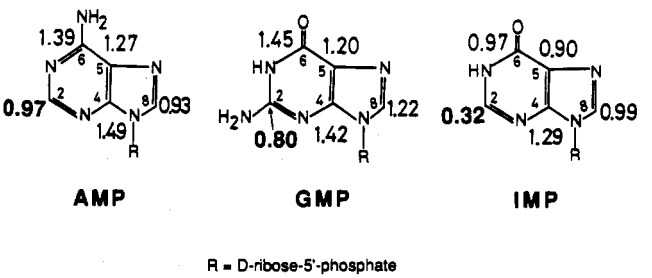

Figure 2. ^{13}C NMR upfield shifts ($\Delta\delta$/ppm) of NMP for 0.05 M NMP–Pt(Me$_2$phen)(en) at pH 8 and 70 °C.[18] The chemical shifts were measured for 0.05 M Pt(Me$_2$phen)(en)–NMP solutions with dioxane as standard. $\Delta\delta = \Delta\delta_{\mathrm{NMP}} - \Delta\delta_{\mathrm{Pt(Me_2phen)(en)–NMP}}$.

The ^{13}C NMR spectra of the 1:1 Pt(Me$_2$phen)(en)–NMP systems at neutral pD clearly showed that the signals for both the Pt(II) complex and NMP were shifted upfield due to the ring current effect[17] arising from the face-to-face stacking between phen and the nucleic base. We see from Figure 2 that the upfield shift ($\Delta\delta$) of the C2 signal of IMP (0.32 ppm) is much smaller than that for GMP (0.80 ppm) and AMP (0.97 ppm). Large differences in the $\Delta\delta$ values between IMP and AMP or GMP were also observed for C5 and C6, whereas the values for the other carbons of NMP and the carbons of Pt(Me$_2$phen)(en) were more or less similar to each other. These upfield shift differences directly show that the six-membered ring of IMP, which is without an amino group, is less favorable for stacking than the corresponding ring of AMP and GMP having it.

These findings indicate that the amino group of AMP, GMP, and CMP contributes to stabilization of the stacking interactions with Pt(L)(en) by serving electrons to the purine or pyrimidine ring to increase its electron density.[19] This is supported by the fact that the amino group has no basic character in the usual pH range with a pK_a value of <2[20] and is desolvated on intercalation.[21] On the assumption that coordinated L is electron-deficient and that the stacking energy is additive, we may infer that the adducts with the guanine–cytosine (G·C) pair is more stable than those with the adenine–thymine (A·T) pair where thymine has no amino group. This is in accordance with the finding that the platinum intercalators show a preference for the G·C pair;[22] the binding constants for calf thymus DNA have been found to be in the order ethidium ion > Pt(phen)(en) > Pt(terpy)(HET) (terpy, 2,2′:6′,2″-terpyridine; HET, 2-hydroxyethanethiolate), and the importance of the positive charge on electrostatic interactions has been described. The log β_1 and $-\Delta H_1°$ values of ethidium bromide for the reaction with NMP's, which are without the DNA structure, are clearly smaller than the corresponding values for Pt(phen)(en) (Table I), which means that the high affinity of ethidium ion for DNA results from various contributions such as greater expanse of the aromatic ring system and lack of site specificity.[22] A·T specific intercalators by Wilson et al.[23] have

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been proposed to bind through a hydrogen bond between the hydroxy group of the intercalators and the C2 carbonyl oxygen of the thymine ring. Extended Hückel molecular orbital calculations for adenine, guanine, hypoxanthine, cytosine, and uracil indicated that the amino substituent supplies electrons to the π orbital of the purine and pyrimidine rings and raises the highest occupied molecular orbital (HOMO) energy level, while the electrons from the carbonyl group occupy the nonbonding orbital.[24] The result further indicates that the presence of an amino group tends to decrease the energy difference between the HOMO of NMP and the lowest unoccupied molecular orbital (LUMO) of Pt(L)(en), favoring the charge transfer between the two rings.[25]

The present findings add to information relevant to thermodynamic selectivity and structure-dependent weak forces that could lead to molecular recognition involving nucleotides[26] and site-specific DNA cleavage reactions.[27]

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Supplementary Material Available: Table listing ^{13}C NMR chemical shifts (δ_c) and upfield shifts ($\Delta\delta$) of NMP for 0.05 M NMP-Pt(Me$_2$phen)(en) at 70 °C (1 page). Ordering information is given on any current masthead page.

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Luminescent Nitridorhenium(V) Complexes

Although photochemical and photophysical studies of transition-metal-main-group complexes containing multiple bonds have been confined primarily to metal-oxo derivatives,[1] there should exist an extensive excited-state chemistry of complexes containing metal-nitrogen multiple bonds. Study of these complexes promises to increase our understanding of the electronic structure of the multiple bond and, in a more practical sense, result in new materials for energy conversion and small-molecule transformation. In our efforts to discover new excited states we have prepared a series of new complexes of the type *trans*-NRe(R$_2$PCH$_2$CH$_2$PR$_2$)$_2$X$^+$ (R = Me, X = Cl, Br; R = Et, X = Cl), which are the first rhenium nitrido complexes to exhibit fluid-solution luminescence at room temperature. These desirable emission properties provide a convenient kinetic handle for exploration of their photophysics. An early lead in our work was provided by several studies on the excited-state properties of nitridoosmium(VI) complexes.[2,3]

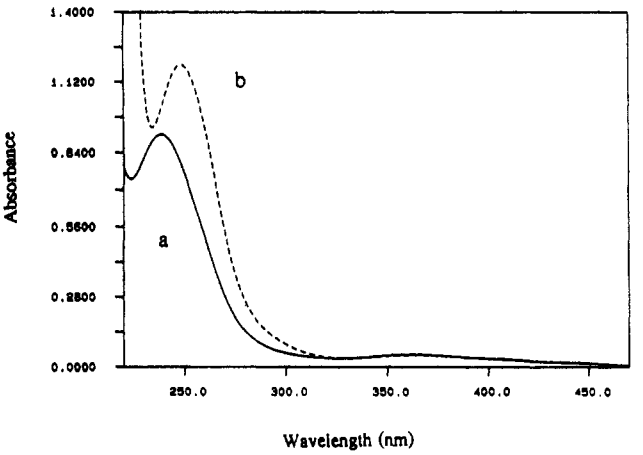

Figure 1. Electronic spectrum for [*trans*-NRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl]Cl in water (a) and after addition of 0.1 M KBr (b) to the same solution.

Preparation of *trans*-NRe(R$_2$PCH$_2$CH$_2$PR$_2$)$_2$Cl$^+$ (R = Me, Et) is accomplished by direct interaction of the reactive precursor NRe(PPh$_3$)$_2$Cl$_2$[4,5] with the appropriate diphosphine ligand in a manner similar to that of Johnson[6] (eq 1). Isolation as the

$$NRe(PPh_3)_2Cl_2 + 2[R_2PCH_2CH_2PR_2] \xrightarrow{EtOH,\ heat} NRe(R_2PCH_2CH_2PR_2)_2Cl^+ + 2PPh_3 + 2Cl^- \quad (1)$$

chloride or hexafluorophosphate salts followed by crystallization from CH$_2$Cl$_2$/Et$_2$O or CH$_3$CN/CH$_3$C$_6$H$_5$ mixtures results in pale yellow to yellow microcrystalline samples[7] that luminesce brilliant green in the solid state. ^{31}P and ^1H NMR and infrared spectral data, in addition to elemental analyses, support the formulations of the complexes.[8]

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(7) A typical preparation for [NRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl]Cl is as follows: 800 mg of NRe(PPh$_3$)$_2$Cl$_2$ (1.01 mmol) was added to 25 mL of ethanol in a 500-mL round-bottom flask in a nitrogen-filled glovebox, and 1.0 g of Me$_2$PCH$_2$CH$_2$PMe$_2$ (5.88 mmol) was added to the flask, and the total volume was brought to 50 mL with ethanol. The flask was securely stoppered, removed from the glovebox, and rapidly transferred to a condenser containing a nitrogen flow with a minimum exposure to air. The mixture was heated to reflux under nitrogen with magnetic stirring. After 90 min, the insoluble, brick-colored starting material had disappeared leaving a yellow-orange solution. Reflux was maintained for another 60 min. The solution was cooled to room temperature, and the volume was reduced by rotary evaporation to about 5 mL. Precipitation was induced by the addition of 500 mL of diethyl ether. The ether mixture was stirred for 60 min, the ether was decanted, and the fluffy yellow solid was collected by suction filtration. The solid was washed with 3 × 25 mL of diethyl ether and dried by suction. The complex was purified by twice reprecipitating from a minimum of chloroform (ca. 25 mL, removing pale orange insoluble impurities by filtration) into diethyl ether (ca. 250 mL). This is followed by recrystallization from 1:5 acetonitrile/toluene under subdued light, with slow evaporation of the acetonitrile. Yield: 480 mg (85%).
(8) Characterization data for [*trans*-NRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl]$^+$ are as follows. UV-visible spectrum in CH$_2$Cl$_2$: λ_{max} = 238 nm (ϵ = 4000 M^{-1}cm^{-1}), λ_{sh} = 257 nm (ϵ = 2980 M^{-1} cm^{-1}), λ_{max} = 362 nm (ϵ = 250 M^{-1} cm^{-1}). Infrared spectrum in CH$_2$Cl$_2$: ν(Re≡N) = 1059 cm^{-1}. ^1H NMR spectrum in CD$_3$CN in ppm, δ: 1.70 (3 H, s, br), 2.00 (3 H, s, br), 2.07 (4 H, t). ^{31}P NMR spectrum in CD$_3$CN: 17.4 ppm vs H$_3$PO$_4$. Anal. Calcd for [NRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl](PF$_6$): C, 21.16; H, 4.75; N, 2.06. Found: C, 21.38; H, 4.72; N, 1.91. The ^1H NMR spectrum revealed a small fraction of toluene present in some samples.

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