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Thermal, Photochemical, and Electrochemical Reactions Involving Binuclear Platinum(II) and -(III) Pyrophosphite Complexes. Reaction Chemistry of $Pt_2(P_2O_5H_2)_4^{4-}$ and the Halide Complexes $Pt_2(P_2O_5H_2)_4X_2^{4-}$

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The bridged binuclear complex $Pt_2(P_2O_5H_2)_4^{4-}$ ($P_2O_5H_2^{2-}$ = $HO(O)POP(O)OH^{2-}$) has recently attracted interest because of its distinctive spectroscopic properties.[2-9] Halogen addition across this biplatinum(II) complex yields axially substituted biplatinum(III) compexes $Pt_2(P_2O_5H_2)_4X_2^{4-}$ (X = Cl, Br, I).[10] With only small added quantities of halogen, the mixed-valence $Pt^{II}Pt^{III}$ complexes $Pt_2(P_2O_5H_2)_4X^{4-}$ can be obtained in the solid state.[11] A simple molecular orbital description of the bonding proposes the orbital occupancies to be $Pt^{II}Pt^{II}$ $(1a_{1g})^2(1a_{2u})^2$, $Pt^{II}Pt^{III}$ $(1a_{1g})^2(1a_{2u})^1$, and $Pt^{III}Pt^{III}$ $(1a_{1g})^2$ (where $1a_{1g}$ and $1a_{2u}$ are $d\sigma$ and $d\sigma^*$), and the electronic transitions between $d\sigma^* \rightarrow p\sigma$ and $d\sigma \rightarrow d\sigma^*$ are assigned on the basis of this model.[12] No reaction chemistry has yet been published interrelating these $Pt^{II}Pt^{II}$, $Pt^{II}Pt^{III}$, and $Pt^{III}Pt^{III}$ complexes. This communication for the first time describes the solution reactions of these binuclear Pt(III) complexes, and shows how this chemistry can be related to the spectroscopic models.

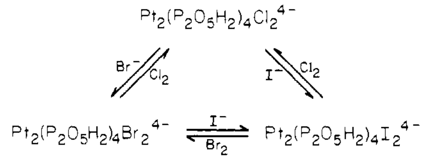
The compounds $Pt_2(P_2O_5H_2)_4^{4-}$ and $Pt_2(P_2O_5H_2)_4Cl_2^{4-}$ are dibasic acids with pK_1 = 3.10 and 4.95 and pK_2 = 6.75 and 7.55, respectively. The monodeprotonated complexes are stable in aqueous solution, but the doubly deprotonated complexes rapidly deposit metallic platinum from solution. Charge differences affect substitution rates since $Pt_2(P_2O_5H_2)_4Cl_2^{4-}$ (pH <4; phosphate buffer and constant ionic strength) does not undergo significant substitution of Cl^- for Br^- or I^-, but $Pt_2(P_2O_5H_2)_3(P_2O_5H)X_2^{5-}$ (X = Cl, Br, I) will undergo replacement at pH = 6.5 of X^- for Y^- (25 °C; X = Cl, Y = Br, I; X = Br, Y = I; X = I, Y = Br).[13] This selective axial substitution is followed spectroscopically by changes in the $(1a_{1g})^2 \rightarrow (1a_{1g})^1(1a_{2u})^1$ ($d\sigma \rightarrow d\sigma^*$) transitions at 282 (X = Cl), 305 (X = Br), and 338 nm (X = I).[10] No mixed halide complex $Pt_2(P_2O_5H_2)_3(P_2O_5H)XY^{5-}$ is formed.

Table I. Thermal and Photochemical Halide Substitution Reactions of $Pt_2(P_2O_5H_2)_4X_2^{4-}$ with Halides Y^-

complex (25 μM)	halide (1 mM)	conditions[a]	time	% substitution
$Pt_2(P_2O_5H_2)_4Cl_2^{4-\,b}$	I^-	thermal	200 min	75
		$h\nu$	70 s	75
	Br^-	thermal	3 h	0
		$h\nu$	60 s	60
$Pt_2(P_2O_5H_2)_4Br_2^{4-}$	I^-	thermal	12 h	1
		$h\nu$	12 min	75
	$Cl^{-\,c}$	thermal	12 h	4
		$h\nu$	12 min	60
$Pt_2(P_2O_5H_2)_4I_2^{4-}$	$Br^{-\,c}$	thermal	3 h	3
		$h\nu$	2 min	95
	Cl^-	thermal	3 d	0
		$h\nu$	15 min	100

[a] 25 °C, pH 1. [b] pH 6. [c] $[Cl^-]$, $[Br^-]$ = 100 mM.

Scheme I



Halide substitution in $Pt_2(P_2O_5H_2)_4X_2^{4-}$ is photochemically accelerated. Comparative thermal and photochemical data are collected in Table I. All replacements show photoenhancement, and the replacement of I^- by Cl^- shows 100% photochemical substitution in 15 min as compared to no thermal reaction after 3d (eq 1). These photochemical reactions use Pyrex glassware

$$Pt_2(P_2O_5H_2)_4I_2^{4-} \xrightarrow[\text{HCl (pH 1)}]{h\nu} Pt_2(pop)_4ICl^{4-} \xrightarrow[\text{HCl (pH 1)}]{h\nu} Pt_2(P_2O_5H_2)_4Cl_2^{4-} \quad (1)$$

and for the case of X = I a sharp cutoff filter (λ > 335 nm).[14] These photochemical substitutions, which show a minimum enhancement of 200 over the thermal rate, are selectively axial and proceed via the observable XY intermediate under pH 1 conditions. The thermal reactions of $Pt_2(P_2O_5H_2)_4X_2^{4-}$ resemble those of the kinetically inert monomeric platinum(IV) complexes. Two explanations are possible to explain the photoenhancement of substitution. Irradiation in the $d\sigma \rightarrow d\sigma^*$ chromophore will produce a $17e^-17e^-$ diradical $(1a_{1g})^1(1a_{2u})^1$ excited state, and if the triplet state is sufficiently long-lived it may show substitution lability analogous to monomeric $17e^-$ radicals.[15] The more likely reason, however, is that the excited state involves X → Pt(III) LMCT character, resulting in a photoinduced $Pt^{II}Pt^{III}$ intermediate $Pt_2(P_2O_5H_2)_4X^{4-}$.[16] Lability in such an intermediate would explain our observed photoenhancement. This pathway parallels that proposed by Taube for platinum(IV) complexes.[17] Photoinduced lability of platinum(IV) complexes proceeds via platinum(III) intermediates, which are formed in a chain process with quantum yields greater than unity.[18] Quantum yield measurements in progress on substitutions in $Pt_2(P_2O_5H_2)_4X_2^{4-}$ should help decide the electronic character of the excited state.

Halogens Y_2 react with $Pt_2(P_2O_5H_2)_4X_2^{4-}$ to exchange X for Y if Y = Cl, Br and X = I, or if Y = Cl and X = Br, I. The reverse reactions involving oxidation of Y^- by X_2 are thermody-

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namically unfavorable. Scheme I shows the thermal replacement reactions that occur with halogens and halides. If small quantities of Y_2 are added to $Pt_2(P_2O_5H_2)_4X_2^{4-}$ the initial formation of $Pt_2(P_2O_5H_2)_4XY^{4-}$ can be verified (eq 2). With interhalogens

$$Pt_2(P_2O_5H_2)_4X_2^{4-} \xrightarrow{Y_2} Pt_2(P_2O_5H_2)_4XY^{4-} \xrightarrow{Y_2} Pt_2(P_2O_5H_2)_4Y_2^{4-} \quad (2)$$

(XY) and $Pt_2(P_2O_5H_2)_4^{4-}$ the first product is $Pt_2(P_2O_5H_2)_4XY^{4-}$ (XY = CH_3I,[10] ICl, IBr, CNBr, CNI), but if excess XY is added the major product is $Pt_2(P_2O_5H_2)_4Y_2^{4-}$ (eq 3).[19] No evidence

$$Pt_2(P_2O_5H_2)_4^{4-} \xrightarrow{CNY} Pt_2(P_2O_5H_2)_4CNY^{4-} \xrightarrow{CNY} Pt_2(P_2O_5H_2)_4Y_2^{4-} + (CN)_2 \quad (3)$$

is found for $Pt_2(P_2O_5H_2)_4X_2$ (X = CH_3, CN, I (from ICl, IBr)), which correlates with $E°(Cl_2/Cl^-) > E°(Br_2/Br^-) > E°(I_2/I^-) > E°((CN)_2/CN^-)$.

Using techniques of Pt(IV) chemistry,[20] we can use a novel method to prepare stable aqueous solutions of the mixed complexes $Pt_2(P_2O_5H_2)_4XY^{4-}$ (X = Cl, Y = Br, I; X = Br, Y = I) in high yield. This complementary redox process[21] involves treating an aqueous mixture of halide (X^-) and $Pt_2(P_2O_5H_2)_4^{4-}$ at low pH with a small quantity of halogen Y_2 (X = Cl, Y = Br, I; X = Br, Y = I) (eq 4).

$$Pt_2(P_2O_5H_2)_4^{4-} + X^- + Y_2 \xrightarrow{\text{pH } 1} Pt_2(P_2O_5H_2)_4XY^{4-} + Y^- \quad (4)$$

At this low pH the solutions are stable since $[Y^-]$ is low and the substitution rate is slow. Respective λ_{max} are ClBr 298 nm (ϵ 5.6 × 10^4), ClI 313 nm (ϵ 4.1 × 10^4), BrI 316 nm (ϵ 5.2 × 10^4). The ^{31}P NMR spectra correspond with the XY compounds formed by eq 2.

Although reversible electrochemistry has not been observed because of electrode adsorption, chemical reduction of $Pt_2(P_2O_5H_2)_4^{4-}$ to $Pt_2(P_2O_5H_2)_4^{6-}$ occurs with Cr(II).[22] Electrochemical oxidation of a solution of $Pt_2(P_2O_5H_2)_4^{4-}$ and X^- (X = Cl, Br, I) at pH 1–2 with a Pt gauze electrode at + 0.8 V vs. Ag/AgCl gives $Pt(P_2O_5H_2)_4X_2^{4-}$. At 0.0 V, or with added H_2, H_3PO_2, or Zn/Hg, the reaction is reversed. For conditions where $[Pt_2(P_2O_5H_2)_4^{4-}] = [Pt_2(P_2O_5H_2)_4X_2^{4-}]$, we find E° (X = Cl) = 0.20, $E°$ (X = Br) = 0.066, and $E°$ (X = I) = −0.146 V vs. SCE. This low potential for oxidation of $Pt_2(P_2O_5H_2)_4^{4-}$ correlates with electron loss from a dσ* HOMO. The one-electron oxidants Ce^{4+} and $IrCl_6^{2-}$ can also be used to effect this oxidation (eq 5), and

$$Pt_2(P_2O_5H_2)_4^{4-} \underset{e^-, -X^-}{\overset{-e^-, X^-}{\rightleftharpoons}} Pt_2(P_2O_5H_2)_4X^{4-} \underset{e^-, -X^-}{\overset{-e^-, X^-}{\rightleftharpoons}} Pt_2(P_2O_5H_2)_4X_2^{4-} \quad (5)$$

a Ce^{4+} titration verifies that $n = 2$ for the oxidation.[23] If we assume an initial l-electron process, removal of a $1a_{2u}$ (dσ*) electron from $Pt_2(P_2O_5H_2)_4^{4-}$ gives $Pt_2(P_2O_5H_2)_4^{3-}$, which with excess X^- will form the mixed-valence complex $Pt_2(P_2O_5H_2)_4X^{4-}$. Since solutions of $Pt_2(P_2O_5H_2)_4X^{4-}$ rapidly disproportionate[11] the product $Pt_2(P_2O_5H_2)_4X_2$ can result either from this reaction or from transfer of a second electron to the oxidant followed by halide ion capture.

We are currently doing kinetic measurements and quantum yield experiments to mechanistically probe these reactions.

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[19] For $Pt_2(P_2O_5H_2)_4CNBr^{4-}$: λ_{max} = 279, 344 nm; ν(CN) = 2152.6 cm^{-1}; ^{31}P NMR δ 26.08 ($^1J(^{195}Pt^{31}P)$ = 2230 Hz), 16.58 ($^1J(^{195}Pt^{31}P)$ = 1993 Hz); ^{195}Pt NMR −4593 ($^1J(^{195}Pt^{31}P)$ = 2224, $^2J(^{195}Pt^{31}P)$ = 102 Hz), −4101 ($^1J(^{195}Pt^{31}P)$ = 1988, $^2J(^{195}Pt^{31}P)$ = 67 Hz). For $Pt_2(P_2O_5H_2)_4CNI^{4-}$: λ_{max} = 294, 356 nm; ν(CN) = 2151.7 cm^{-1}; ^{31}P NMR δ 19.96 ($^1J(^{195}Pt^{31}P)$ = 2219 Hz, 15.40 ($^1J(^{195}Pt^{31}P)$ = 2006 Hz); ^{195}Pt NMR δ −5087 ($^1J(^{195}Pt^{31}P)$ = 2218, $^2J(^{195}Pt^{31}P)$ = 92 Hz), −4028 ($^1J(^{195}Pt^{31}P)$ = 1934, $^2J(^{195}Pt^{31}P)$ = 57 Hz). For $Pt_2(P_2O_5H_2)_4BrCl^{4-}$: ^{31}P NMR δ 27.42 ($^1J(^{195}Pt^{31}P)$ = 2151 Hz), 24.38 ($^1J(^{195}Pt^{31}P)$ = 2153 Hz). For $Pt_2(P_2O_5H_2)_4ICl^{4-}$: ^{31}P NMR δ 26.47 ($^1J(^{195}Pt^{31}P)$ = 2236 Hz), 19.46 ($^1J(^{195}Pt^{31}P)$ = 2175 Hz).

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Virtual Transition State for the Acylation Step of Acetylcholinesterase-Catalyzed Hydrolysis of *o*-Nitrochloroacetanilide[1]

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Acetylcholinesterase (AChE) catalysis[2] occurs via an acylenzyme mechanism involving nucleophilic attack by serine on the substrate, with general acid–base assistance by histidine. Rosenberry[2,3] suggested that small solvent deuterium isotope effects (<1.5) and low pK_a's (<6) for k_{cat}/K_m of the AChE-catalyzed hydrolyses of neutral acetate esters arise because a pH-insensitive, nonchemical step (induced fit) preceding general acid–base catalysis figures prominently in rate determination. The low pK_a's were considered to result from reduction of the intrinsic pK_a = 6.3 of the catalytic histidine by a kinetic term containing the rate constant of the pH-insensitive step (vide infra). When more than a single elementary step contributes to rate determination, the observed transition state is a virtual transition state,[4,5] for which phenomenological descriptors of structure, such as solvent isotope effects, contain weighted contributions from the requisite elementary step transition states. In this communication we show that the acylation transition state of the AChE-catalyzed hydrolysis of *o*-nitrochloroacetanilide[6] (ONCA) is a virtual transition state and dissect the virtual transition state into its component transition states.

Figure 1 shows that, as for Rosenberry's ester substrates,[3] pL-rate profiles (L = H, D) for the acylation step of AChE-catalyzed hydrolysis of ONCA yield small solvent isotope effects and low pK_a's. The least-squares calculated pK_a's are 5.77 ± 0.02 and 6.17 ± 0.02 in H_2O and D_2O, respectively, and the isotope effect on the least-squares extrapolated limiting velocity is 1.357 ± 0.007. Figure 2 shows that the partial solvent isotope effect determined in mixed H_2O–D_2O buffers varies in a bowing upward manner with increasing mole fraction of deuterium, similar to the dependence reported by Hogg et al.[7] for acylation of AChE by *p*-nitrophenyl acetate. The general expression for the dependence of rate constant on mole fraction of deuterium in the solvent is given by the Gross–Butler equation:[8-10]

$$k_n = k^{H_2O} \frac{\prod_j (1 - n + n\Phi_j^{T})}{\prod_i (1 - n + n\Phi_i^{R})} \quad (1)$$

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