formed from CO + H_2 at 152 °C, but at 182 °C the catalyst was active, giving C_1–C_7 hydrocarbon mixtures at a conversion of ≥15% and a rate of ~8 molecules of CO converted/(Co atom h). *Most strikingly, almost no C_2 or C_3 hydrocarbons were produced, the main product being n-butane, with the C_4–C_7 mixture constituting ≃70% of the hydrocarbon product* (Figure 3). The deviation from Schulz–Flory behavior (Figure 2) and the sharp product concentration profile (~25% C_4, ~0% C_8) confirm a shape selectivity different from that observed with the A-type zeolite. The size, structure, and environment of the catalytically active species are evidently important in addition to the molecular-sieving character of the zeolite pores.

We believe that these results may portend a challenging new chemistry of stabilized metal clusters in the unique solvent-like environments of zeolite pores and open the way to new catalytic science and technology to meet some of our most pressing needs for synthesis gas conversion into fuels and petrochemical substitutes.

Acknowledgment. We thank A. W. Sleight, E. Gleason, and P. Gajardo for helpful discussions.

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(12) Metal vapor reduction of exchangeable cations in zeolite A was first performed by R. M. Barrer and J. L. Whiteman [*J. Chem. Soc. A*, 19 (1967)], who reduced Ag^+ in AgA by Hg vapor. Most of the reduced Ag was reported to have escaped from the zeolite intracrystalline channel system and agglomerated to form large particles external to the zeolite micropores. Co^0 is potentially a better catalyst than Ag^0 and is also much less mobile in zeolite A than Ag^0, but Hg vapors are not sufficiently effective as a reducing agent for Co^{2+} ions. Therefore, we have chosen CoA with Cd as the reducing agent.
(13) Only the catalyst recovered from expt 2 (Table I) showed infrared Co–CO absorption bands (Figure 1). It is noteworthy that no particular care was taken to protect the catalyst from the ambient atmosphere.
(14) Recently, the crystal structure of Cd(II)-exchanged zeolite A evacuated at 500 °C was reported: L. B. McCusker and K. Seff, *J. Am. Chem. Soc.*, **101**, 5235 (1979). Upon exposure of the zeolite to Cd vapor, Cd^+ and Cd_2^{2+} species were formed within the cages. We believe that in our case a similar system might have formed and Cd species, whether alone or combined with Co,[12] could participate in the catalytic action, as predicted by McCusker and Seff.
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Platinum(II) Anti-Tumor Agents. A New Class of Intrastrand Cross-Linking Models Exhibiting Significant Intracomplex Base–Base Interactions

Sir:

The anti-tumor agent *cis*Pt {*cis*-$[(NH_3)_2PtCl_2]$} has exhibited remarkable clinical utility against a broad spectrum of human tumors.[1] Since the discovery of the anti-tumor activity of Pt(II) compounds,[1] a considerable amount of research has focused on elucidating the mechanism of activity of these novel drugs. Almost all of the evidence accumulated to date implicates DNA of the tumor cell as the molecular target of *cis*Pt.[2] Although numerous reaction sites are available on a polynucleotide,[3] strong evidence exists that at low Pt/DNA ratios (conditions best approximating in vivo levels) the guanine bases are attacked preferentially.[3] A compelling and chemically feasible, but unproven, explanation for the requirement of two cis positions on all active Pt(II) anti-tumor agents is that an intrastrand cross-link between two guanosine bases is the critical lesion. Evidence for such cross-linking in polynucleotides has been reported.[2-4]

An alternative explanation for the requirement of two cis leaving groups is that an N(7),O(6) chelate is formed between the guanine base and the Pt(II) center.[5] This hypothesis is attractive since, by involving the 6-oxo group in the interaction with an electrophilic center, the model affords a mechanism for base mispairing and thereby an explanation for the effectiveness of the Pt(II) agent.[5] However, no definitive structural evidence exists for such a chelation mode in Pt(II) chemistry.[6]

In contrast, intrastrand cross-linking models containing Pt(II) and guanosine[7-8] (class I) or the dianion of inosine 5′-monophosphate (5′-IMP)[9-12] (class II) are known. However, quite different structural features are found in these two classes of complexes (Table I). The molecular structures of the closely related bis(guanosine) complexes[7-8] contain no unusual features. On the other hand, the molecular structures of the bis(5′-IMP) complexes show appreciable intracomplex base–base interactions.[9-12] Evaluation of these interactions in the 5′-IMP systems is complex since the compounds are isomorphous with the monosodium salt of 5′-IMP (NaH-IMP),[13] and the crystal structure (particularly the binding of the Na^+ counterion) is important.

In this report, we describe the preparation and structure of the complex $[(tn)Pt(Me\text{-}5'\text{-}GMP)_2]$, where tn = trimethylenediamine and Me-5′-GMP is the phosphate methyl ester of guanosine 5′-monophosphate (Figure 1). This neutral complex lacks any charge compensating counterion, allowing a freer environment in the solid than in the Pt(II)-5′-IMP

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Table I. Some Intramolecular Parameters in a Variety of Bis(nucleoside)Pt(II) and Bis(nucleotide)Pt(II) Complexes

compd[a]	interligand N(7)···N(7) distance, Å	dihedral angle between purine planes, deg	interligand O(6)···C(8) contact, Å	% Pt	ref
cis-[(en)Pt(Guo)$_2$]$^{2+}$	2.71	71		100	7
cis-[(NH$_3$)$_2$Pt(Guo)$_2$]$^{2+}$	2.7	74		100	8
NaHIMP	3.48	22	3.46	0	13
cis-[(tn)Pt(5′-IMP)$_2$]$^{2-}$	2.93 (2)	38.2 (8)	3.02 (2)	~74	12
cis-[(NH$_3$)$_2$Pt(5′-IMP)$_2$]$^{2-}$	2.88 (1)	40.7 (5)	2.99 (1)	~86	11
cis-[(tn)Pt(Me-5′-GMP)$_2$]	2.86 (1)	39.6 (6)	2.96 (1)	100	this work

[a] Abbreviations: Guo, guanosine; NaHIMP, the monosodium salt of inosine 5′-monophosphate; 5′-IMP, the dianion of inosine 5′-monophosphate; Me-5′-GMP, the monoanion of the methyl ester of guanosine 5′-monophosphate; en, ethylenediamine; tn, trimethylenediamine.

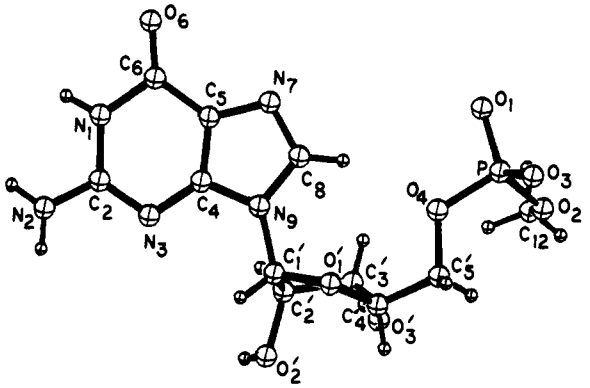

Figure 1. Molecular structure and atomic numbering scheme for the phosphate methyl ester of guanosine 5′-monophosphate(Me-5′-GMP).

complexes. The Me-5′-GMP ligand is a closer model for a polynucleotide unit than either guanosine or 5′-IMP. [(tn)Pt(Me-5′-GMP)$_2$] was prepared by the slow evaporation of a stoichiometric, aqueous (pH 7) solution containing Na(Me-5′-GMP) and "[(tn)Pt(H$_2$O)$_2$]$^{2+}$" (prepared in situ from tnPtI$_2$ using AgNO$_3$). Crystals of [(tn)Pt(Me-5′-GMP)$_2$]·11H$_2$O are tetragonal (space group $P4_322$), with $a = b = 12.317$ (2), $c = 29.449$ (8) Å; $Z = 4$. Anal. Calcd: C, 24.62; H, 5.12; N, 13.78. Found: C, 25.09; H, 5.18; N, 13.44. A structural model, obtained by conventional crystallographic methods, has been refined (employing anisotropic thermal parameters) to a final R value of 7.9% and a final weighted R value of 4.7%.[14] The nearly square-planar coordination geometry for [(tn)Pt(Me-5′-GMP)$_2$] is illustrated in Figure 2. A crystallographic twofold axis passes through the Pt atom and the central carbon atom of the tn ligand.[15] Each Me-5′-GMP monodentate ligand coordinates to Pt through N(7) on the purine ring; coordination to N(7) of guanosine, 5′-IMP, and 5′-GMP is a well-established primary metal-binding mode.[7-12,16] We also show in Figure 2 an intramolecularly hydrogen-bonded water molecule, W(3); this water molecule and the intracomplex O(phosphate)···H—O—H···O(6)(base) hydrogen-bonding scheme are also common to the Pt(II)-5′-IMP complexes.[9-12]

The most important structural aspect of [(tn)Pt(Me-5′-GMP)$_2$] is a highly significant intracomplex base-base interaction, dominated by O(6)···imidazole ring contacts between twofold related ligands (Figure 2). Notable among these contacts is a very short O(6)···C(8) contact (Table I). Thus, *in all of the known instances of cis-coordinated, 6-oxopurine nucleotide complexes of Pt(II), there is a highly significant intracomplex, interbase interaction, even in the absence of lattice effects.*

The class I guanosine complexes have no favorable intracomplex base-base interaction.[7-8] However, there is a significant *intercomplex* interaction between parallel (mean separation 3.3 Å) purine bases, which includes notable base-base overlap reminiscent of the base stacking modes found in free guanosine and inosine.[17] In the structure of NaHIMP,[13] the dominant internucleotide interaction involves substantially nonparallel molecules and is sugar-base in character [utilizing the sugar ring oxygen atom O(1′) in particular].[13,18] However, in class II, the introduction of significant amounts of Pt(II) into the NaHIMP structure causes very noticeable changes to take place.[9-12] While there are still remnants of a weak sugar-base internucleotide interaction, there is a rather dramatic increase in the *intracomplex* base-base interaction (Table I).

It seems possible then that the apparently normal molecular structure of the guanosine complexes may, in fact, result from highly favorable intercomplex base-base stacking in the solid state. The structures of [(tn)Pt(Me-5′-GMP)$_2$] and the Pt-5′-IMP systems strongly suggest, however, that intracomplex base-base interactions may be intrinsic to *cis*-bis(nucleoside)- and *cis*-bis(nucleotide)Pt(II) complexes for 6-oxopurine bases when intercomplex base-base stacking is precluded by the crystal structure. It is clear that more structural investigations are needed to determine the importance of such intracomplex base-base interactions.

Since intercomplex base stacking is improbable in dilute solution, particularly for charged complexes, intracomplex base-base interactions may also be present in solution. Recent

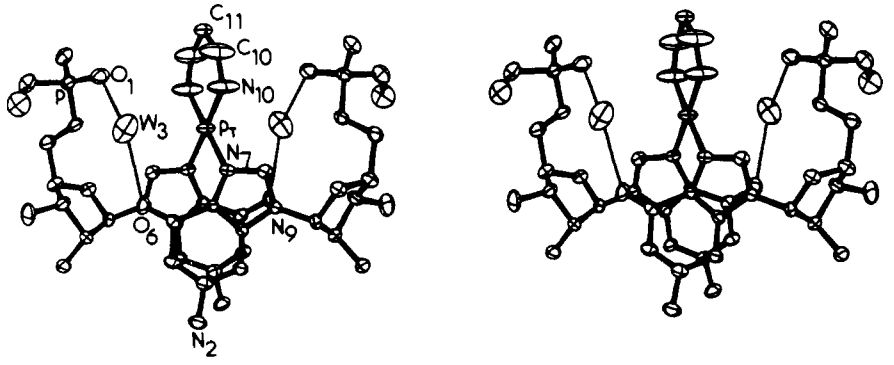

Figure 2. A stereoview of the molecular structure of (tn)Pt^{II}(Me-5′-GMP)$_2$. The molecular and crystallographic twofold axis lies vertically on the page.

CD work[19] indicates that some bis(nucleotide) complexes of Pt(II) exhibit enhanced Cotton effects, similar in nature to the enhancement of the CD spectra of polynucleotides induced by low levels of *cis*Pt.[20-22] If the intracomplex base-base interactions found in this and previous studies reflect binding in the *cis*Pt-DNA complex, then large local distortions in the DNA structure would occur since the base-base overlap found here is dramatically different from that postulated for the various forms of DNA.[18,23]

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Supplementary Material Available: Tables of atomic coordinates and thermal parameters and structure factor amplitudes of [(tn)-Pt(Me-5′-GMP)$_2$] (20 pages). Ordering information is given on any current masthead.

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Gas-Phase Heats of Formation of $C_2H_5^+$ and $C_3H_7^+$

Sir:

The $C_2H_5^+$ and $C_3H_7^+$ radical cations are among the most ubiquitous and important alkyl ions encountered in mass spectrometry. It is therefore surprising that there should still be a question concerning their gas-phase heats of formation.

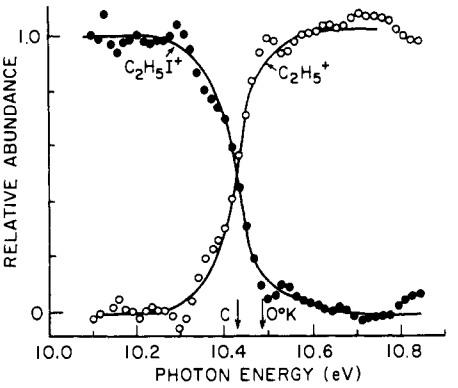

Figure 1. The breakdown diagram in the vicinity of the $C_2H_5^+$ onset. The arrow labeled C points to the crossover point, while the arrow labeled 0 K points to the calculated 0 K onset.

Yet this appears to be the case. Recently, Houle and Beauchamp[1] investigated the photoelectron spectra (PES) of a series of alkyl radicals. From these data, they derived heats of formation of the corresponding ions. These values are based on the heats of formation of the neutral radicals and on the assumption that the ion and neutral structures are sufficiently similar so that an adiabatic ionization energy can be obtained from the PES. Of course, the shape of the PES gives some indication as to whether this latter assumption is justified.

Ionic heats of formation can also be determined by dissociative photoionization of molecule whose neutral heat of formation is well established. The pitfalls in this approach are ion-pair formation, kinetic shift, and the presence of a reverse activation energy.

This communication reports on a photoionization and photoion-photoelectron coincidence (PIPECO)[2] study of $C_2H_5^+$ and $C_3H_7^+$ formation from C_2H_5I and C_3H_7I, respectively. The onset for $C_2H_5^+$ from ethyl iodide was investigated with particular care. The kinetic energy release was measured[3] and found to approach 0 at the dissociation onset, thereby making a significant reverse activation energy very unlikely. The I atom loss is the first dissociation event and it was found to be fast, thereby eliminating a kinetic shift in the onset. Finally, the onset was determined by both photoionization and PIPECO. In the latter experiment, the ion is measured in delayed coincidence with zero energy electrons. Therefore ion-pair formation ($C_2H_5^+ + I^-$) is not observed because the time correlation between $C_2H_5^+$ and I^- is different from that in $C_2H_5^+$ and its electron. Figure 1 shows the breakdown diagram in the vicinity of the $C_2H_5^+$ onset obtained by collecting $C_2H_5I^+$ and $C_2H_5^+$ ions in coincidence with threshold electrons. Our onset in a mass analyzed photoionization scan of $C_2H_5^+$ was 10.42 eV which agrees with the 10.42 ± 0.05 eV onset quoted by Akopyan et al.[4] These onsets are in agreement with the breakdown curve results suggesting that ion-pair processes are not very important.

The crossover point at 10.43 eV in Figure 1 is by definition the energy at which half of the $C_2H_5I^+$ ions have sufficient energy to dissociate. A 0 K onset can be calculated taking into account the internal thermal energy in ethyl iodide at 200 K. It has been amply demonstrated[5] that thermal vibrational and rotational energy in the precursor molecule is available for dissociation. With these assumptions, a 0 K onset of 10.49 eV is calculated. Using the 0 K heats of formation for C_2H_5I and I given in Table I, the 0 K heat of formation of $C_2H_5^+$ is calculated to be 218.2 ± 1.0 kcal/mol.

To convert this value to a 298 K heat of formation, we consider the fundamental equation:

$$2C(s) + {}^5/_2H_2 \rightarrow C_2H_5^+ + e^- \qquad (1)$$

The heat reaction is by definition the heat of formation of

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