of the substitution patterns in ring A, the most potent are the compounds with a 12α-OH function (trichilin B type) which are active at 200 ppm; this is followed by the 12β-OH compounds, 300 ppm, and then the 12-desoxy type, e.g., trichilin D, 400 ppm, and 12α-acetoxy compounds, also 400 ppm. Acetoxylation or ketonization of 7-OH or ketonization at C-12, i.e., **3**/**4** or trichilin C (**5**), renders the compounds inactive. Feeding of trichilin A over a 10-day period to the third instar larvae of *S. eridania* killed the insects. The trichilin structures are too complex to be synthesized on a practical scale. However, their potent activities, comparable to azadirachtin,[16] should be noted.[17]

(16) Zanno, P. R.; Miura, I.; Nakanishi, K.; Elder, D. *J. Am. Chem. Soc.* **1975**, *97*, 1975 and references cited therein. The azadirachtin molecule again is far too complex to be synthesized practically. However, the leaves and fruits of the neem tree from which it was isolated have strong insect antifeedant activity and, in fact, cultivation of the neem tree is under serious consideration.[16a] Also the First International Conference on the neem tree was held in Germany, Aug 1980, because of its potential practical use in pest insect control.

(17) Supported by NIH Grant AI 10187.

New Reaction Chemistry of *cis*-Diammineplatinum(II) with α-Pyridone. Crystalline Relatives of the α-Pyridone Blue

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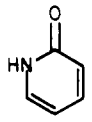
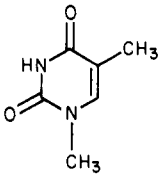
The platinum blues are a family of compounds that have generated much current interest.[1-7] To date, only *cis*-diammineplatinum α-pyridone blue (**1**, Figure 1) has been fully


α-pyridone


1-methylthymine

characterized structurally.[2] Studies on this and related *cis*-diammineplatinum blues strongly suggest that they are all mixed valent, metal-metal bonded, amidate-bridged oligomers.[2-4] Although several nonblue crystalline products (**2**-**4**, Figure 1) have been isolated[8-10] from reaction mixtures that ultimately produce *cis*-diammineplatinum pyrimidine blues, an interesting subclass known to have antitumor properties,[11] no crystals of the pyrimidine blues themselves have yet been obtained.

Here we report the syntheses and structures of three new, nonblue compounds (**5**-**7**, Figure 2) obtained in the reaction of *cis*-diammineplatinum(II) with α-pyridone. The most striking compound is the yellow head-to-head "tetramer" **7**, platinum oxidation state 2.0, which has a geometry nearly identical with that of the α-pyridone blue **1**, average platinum oxidation state 2.25. The longer Pt-Pt distances in **7** are consistent with and strongly support the previous analysis of the electronic structure of **1**. Unlike **7**, the head-to-head 1-methylthyminato complex **4** is only a dimer, and the difference between these two structures provides some insight into the question of why a 1-methylthyminate blue analogous to **1** has not yet been crystallized. The present work also demonstrates that the crystalline complexes previously obtained in the reaction of *cis*-diammineplatinum(II) with 1-methylthymine also form in its reactions with α-pyridone. In particular, there is a close correspondence in molecular geometry between the head-to-tail 1-methylthyminato (**2**) and α-pyridonato (**5**) dimers, the bis(1-methylthyminato) (**3**) and bis(2-hydroxypyridine) (**6**) complexes, and the head-to-head compounds **4** and **7**. The new reaction chemistry found for *cis*-diammineplatinum(II) with α-pyridone, a pyrimidine analogue, provides a foundation for understanding the more complex chemistry that leads to the platinum pyrimidine blues and also expands the list of possibilities for the interaction of the antitumor drug *cis*-$[Pt(NH_3)_2Cl_2]$ with cyclic amides such as those present in the G, C, and T bases of DNA.

Table I. Geometric Comparison of *cis*-Diammineplatinum Complexes

compd	distance, Å				dihedral angle, deg[a]		ref
	Pt-Pt	Pt-NH_3	Pt-N	Pt-O	τ	ω	
1	2.77 2.88	2.06 (av)	2.05 (av)	2.04 (av)	27.4	22	2
2	2.97	2.05 (av)	2.04 (av)	2.04 (av)	36.1	14	8
4	2.91	*b*	*b*	*b*	29.5	1	9
5	2.90	2.05 (av)	2.03	2.02	28.9	13	*c*
6		2.04	2.03				*c*
7	2.88 3.13	2.05 (av)	2.05 (av)	2.04 (av)	30.0	21	*c*

[a] τ is the tilt angle between adjacent platinum coordination planes, and ω is the average torsion (or twist) angle about the Pt-Pt vector (see ref 2). [b] Values not reported. [c] This work.

Crystals of the head-to-tail dimer **5**, $[Pt(NH_3)_2(C_5H_4ON)]_2(NO_3)_2 \cdot 2H_2O$, were isolated in 40-60-mg quantities by cooling the filtrate of the solution from which the α-pyridone blue crystals were harvested[3] for an additional 12-24 h at 3 °C. The light yellow compound was characterized by analytical and spectroscopic data[12] and a complete X-ray crystal structure analysis.[13]

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(12) Chemical and spectroscopic data. Anal. Calcd for $Pt_2C_{10}H_{24}N_8O_{10}$ (**5**): C, 14.89; H, 3.00; N, 13.89. Found: C, 14.85; H, 3.06; N, 13.83. NMR (Me_2SO-d_6) δ 8.10 (d, Pt satellites, H_6), 7.24 (t, H_4), 6.42 (t, H_3, H_5), 4.54, 4.39 (br, overlapping peaks, Pt satellites, NH_3). Anal. Calcd for $PtC_5H_{11}N_3OCl_2$ (**8**): C, 15.20; H, 2.81; N, 10.63; Cl, 17.94. Found: C, 15.15; H, 2.72; N, 10.57; Cl, 17.72. NMR (Me_2SO-d_6) δ 8.28 (d, Pt satellites, H_6), 7.80 (t, H_4), 6.88 (m, H_3, H_5), 4.48 (br t, Pt satellites, NH_3), 4.24 (s, OH).

(13) X-ray analysis. Compound **5** crystallized in the monoclinic system (space group $C2/c$) with the following cell parameters: a = 15.440 (4), b = 14.350 (2), c = 10.667 (1) Å; β = 118.09 (2)°, ρ_{obsd} = 2.56 (2), ρ_{calcd} = 2.57 g/cm³ for Z = 4 formula units. The structure was solved by standard heavy-atom Patterson and Fourier methods using 2402 unique reflections collected with Mo Kα (λ = 0.7107 Å) radiation out to 2θ = 55° on a Nonius CAD-4F diffractometer. Refinement of the absorption corrected data with all atoms assigned anisotropic temperature parameters, except hydrogens which were refined isotropically with constraints, has converged to a value of 0.033 for the discrepancy index $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. Compound **6** also crystallizes in the monoclinic system (space group $C2/c$) with cell parameters a = 9.072 (2), b = 22.875 (3), c = 8.003 (1) Å, β = 109.24 (1)°, ρ_{obsd} = 2.08 (2), ρ_{calcd} = 2.07 g/cm³ for Z = 4 formula units. The structure was solved as above, using 1802 unique reflections; the refinement converged at R_1 = 0.038. Compound **7** crystallizes in the monoclinic system (space group $P2_1/n$) with the following cell parameters: a = 9.158 (1), b = 9.907 (1), c = 21.405 (1) Å; β = 96.98 (8)°, ρ_{obsd} = 2.67 (2), ρ_{calcd} = 2.66 g/cm³ for Z = 4 formula units. The structure was solved as above using 4417 unique reflections and refinement has converged at R_1 = 0.038. Atomic positional and thermal parameters for all three compounds are provided as supplementary material. Full details will be reported at a later date.

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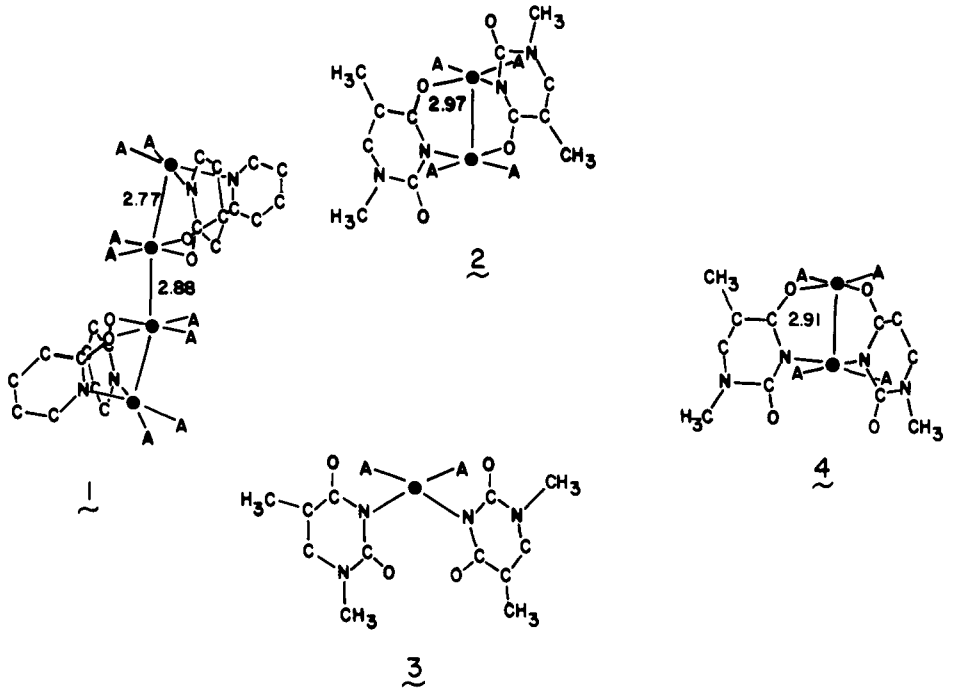

Figure 1. Sketches of the structures of *cis*-diammineplatinum α-pyridone blue (**1**),[2] the head-to-tail isomer of bis(μ-1-methylthyminato-N^3,O^4)bis(cis-diammineplatinum(II)) (**2**),[8] bis(1-methylthyminato-N^3)diammineplatinum(II) (**3**),[10] and head-to-head isomer of bis(μ-1-methylthyminato-N^3,O^4)bis(*cis*-diammineplatinum(II)) (**4**).[9] Platinum atoms are shown as filled circles, ammonia ligands are designated by the letter A, and double bonds and charges are omitted. Compounds **1**–**4** have respective charges of +5, +2, 0, and +2.

Compound **6**, *cis*-$[Pt(NH_3)_2(C_5H_5ON)_2]Cl_2$, was obtained as a minor component from the reaction of *cis*-dichlorodiammineplatinum(II) with α-pyridone as follows. A suspension of 6.67 mmol of *cis*-$[Pt(NH_3)_2Cl_2]$ was stirred with 15 mmol of α-pyridone in 180 mL of water for 24 h at 65 °C. The volume of the resulting amber solution (pH 3.5) was reduced with a rotoevaporator at 50 °C to 15 mL, cooled to ice temperature, and filtered to remove unreacted starting material (0.5 g of *cis*-$[Pt(NH_3)_2Cl_2]$). Continued evaporation followed by the addition of chloroform yielded a light beige product which was filtered and dried (1.7 g). Recrystallization of this material from water gave white needles that were found from analytical and spectroscopic data to be *cis*-chloro(2-hydroxypyridine)diammineplatinum(II) chloride (**8**).[12] Reverse-phase high-performance LC studies of the reaction solution showed **8** to be the major product. Colorless crystals of **6**, found by high-performance LC to comprise less than 5% of the crude product, were obtained by fractional crystallization from water–acetonitrile and identified by X-ray crystallographic analysis.[13] Several other products can also be isolated from the reaction, as will be reported at a later date. The head-to-head complex **7**, $[Pt_2(NH_3)_4(C_5H_4ON)_2]_2(NO_3)_4$, was obtained by adding a solution containing 0.1 mmol of $[Pt_2(NH_3)_4(OH)_2](NO_3)_2$[14] dissolved in 8 mL of water to 0.1 mmol of α-pyridone in 1 mL of water, adjusting the pH to 10 with 1 N NaOH, warming the solution to 37 °C for 24 h (final pH 7.5), and evaporating the solution in air for 2 days. Approximately 80–90% of the resulting crystals were the dihydroxo-bridged starting material. The remaining 10% were found to be the head-to-tail dimer (vide supra). A very small amount of **7** was obtained as greenish yellow needles in 1% yield from the filtrate, intermixed with crystals of **5**. The structure of **7** was determined crystallographically.[13] Attempts to obtain this compound in greater quantities are currently in progress. It should be noted that the pH must be kept around neutrality to avoid the formation of the partially oxidized α-pyridone blue.

Figure 2 shows ORTEP drawings of the three newly characterized α-pyridone complexes, and Table I compares their geometries with those of the previously reported compounds **1**, **2**, and **4**. Particularly interesting is the comparison of the α-pyridone blue **1** with the head-to-head α-pyridone tetramer **7**. The partial metal–metal bonding in the mixed valence blue species results in shorter distances both for the bridged (2.77 vs. 2.88 Å) and, especially, for the unbridged (2.88 vs. 3.13 Å) Pt–Pt vectors. It is noteworthy that the dimeric head-to-head 1-methylthyminate complex **4**[9] does not associate into a tetramer in the solid state through stacking and N—H··O hydrogen-bonding interactions as does the α-pyridonate analogue **7**. Its failure to do so may explain why single crystals of a 1-methylthyminate blue have yet to be synthesized. Intramolecular nonbonded repulsions involving the methyl groups of the ligand and the ammines of an adjacent platinum coordination plane would render a structure analogous to **1** unstable. Possible alternative structures for the noncrystalline, oligomeric *cis*-diammineplatinum pyrimidine, α-pyridone, and related blues have been thoroughly discussed elsewhere.[1,4,9]

Crystals of the head-to-tail dimer inevitably form in the syntheses of the α-pyridone and 1-methylthymine platinum blues. These compounds have very similar structures (compare the results for **2** and **5** in Figures 1 and 2 and Table I), with canted and twisted platinum coordination planes resulting mainly from nonbonded intramolecular steric factors.[2,8] One difference is that, unlike **2**, the Pt–N and Pt–O bond lengths in **5** are identical for the two different platinum coordination planes which are related to one another by a twofold symmetry axis.

The structure of the neutral molecule **3** is presumably as drawn in Figure 1 although its details are not yet available.[10] The platinum atom is bonded to the deprotonated N-3 atoms of two 1-methylthyminate ligands. By contrast, compound **6** is a cation in which two α-pyridone ligands coordinate to platinum through the pyridine nitrogen atom. The *o*-hydroxyl groups are hydrogen bonded to chloride ions in the crystal lattice. Thus the minor tautomer[15] in water of α-pyridone, 2-hydroxypyridine, is stabilized in this complex and, presumably, in the mono-2-hydroxypyridine

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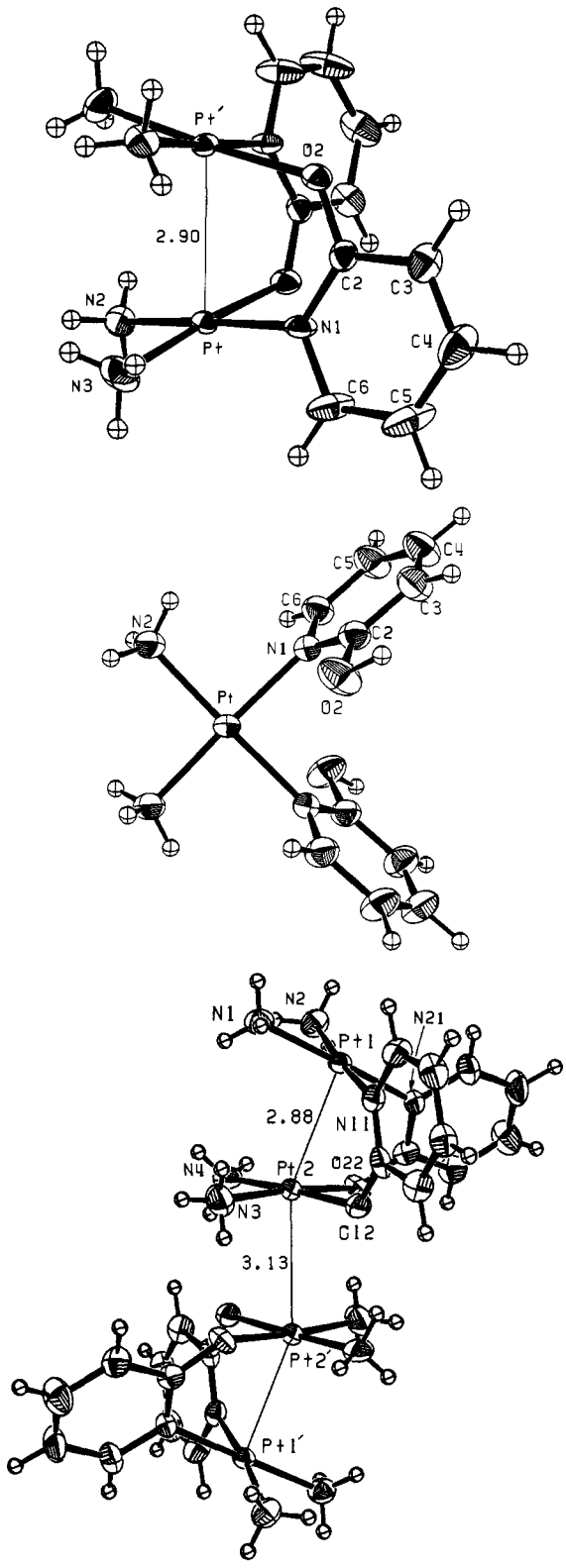

Figure 2. ORTEP drawings of three structures determined in the present study, head-to-tail bis(μ-α-pyridonato-*N*,*O*)bis(*cis*-diammineplatinum(II)) nitrate dihydrate (**5**), bis(2-hydroxypyridine)diammineplatinum(II) chloride (**6**), and head-to-head bis(μ-α-pyridonato-*N*,*O*)bis(*cis*-diammineplatinum(II)) nitrate (**7**). For clarity, hydrogen atoms are depicted as arbitrary spheres with $B = 1$ Å^2. In **5** there is a crystallographic twofold axis relating the two halves of the cation; in **6**, the platinum atom lies on a crystallographic twofold axis; in **7**, the two halves of the tetramer are related by a crystallographic inversion center.

adduct (**8**).

Acknowledgment. This work was supported by National Institutes of Health Research Grant CA-15826. We also thank Engelhard Industries for a loan of K_2PtCl_4 and James Hannon for experimental assistance.

Supplementary Material Available: Atomic positional and thermal parameters for compounds **5**-**7** (2 pages). Ordering information is given on any current masthead page.

Structure of the Reaction Barrier in the Selenoxide-Mediated Formation of Olefins

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The use of selenoxide-forming procedures has become very popular as a means of introducing the double bond into complex organic structures via a stereospecific, syn elimination.[1] These methods appear to have been almost indispensible in the synthesis of many natural products[2] where reaction of compounds with low-activation requirements have their greatest utility. The mechanistic course of the analogous reaction of sulfoxides, which have somewhat higher activation demands, has been studied in these laboratories by application of kinetic deuterium isotope effect criteria.[3] Through measurement of the temperature dependence of k_H/k_D it was shown that the normal thermolysis of sulfoxides takes place via a planar, 5-membered, pericyclic transition state.[4] This investigation of the course of thermolysis of selenoxides was undertaken with the objective of ascertaining the origins of the diminished activation requirements[1d,f] when selenium replaces sulfur in corresponding reaction transition states.

Cinnamyl alcohol was converted to 3-phenyl-2-deuteriopropanol (**1**) in near quantitative yield by the procedure of Hochstein and Brown.[5] This was converted to the tosylate and thence to the phenyl selenide (**2**) utilizing a method described by Clark and Heathcock.[6] When **2** was ozonized to its selenoxide **3** and this in turn decomposed unimolecularly[1d,f] in an inert solvent at temperatures within the range 40-85 °C, the product composition of allybenzenes (in accord with eq 1) could be directly related

$$2 + O_3 \longrightarrow \underset{\underset{O}{|}}{PhCH_2{-}CHD{-}CH_2{-}SePh} \xrightarrow{\Delta} \underset{3}{} \quad \begin{Bmatrix} PhCH_2{-}CH{=}CH_2 \\ PhCH{-}CD{=}CH_2 \end{Bmatrix} + \begin{Bmatrix} PhSeOD \\ PhSeOH \end{Bmatrix} \qquad (1)$$

(mixture analyzed for deuterium content) (recovered as $PhSeO_2H$ and $PhSe_2$)

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