formation is indicated by extensive studies in these laboratories to be described elsewhere which show that the preference is maintained for the full eicosanoid side chains with $\Delta^{12,13}$ cis and $\Delta^{14,15}$ either cis or trans.[20] Clearly the PG synthetase must control stereochemistry in the face of this intrinsic kinetic bias either by preventing the initiating carbon radical from assuming a conformation analogous to **15** or by forcing a conrotatory closure.[21]

Supplementary Material Available: ^{1}H NMR, IR, UV, and MS data for new compounds (3 pages). Ordering information is given on any current masthead page.

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(21) This research was assisted financial by a grant from the National Science Foundation. We thank Drs. John O. Albright and Claude Le Drian for providing samples of the alcohol corresponding to **4**.

Correlation between Metal–Metal Distances and Optical Spectroscopy in the Platinum Blues: Synthesis, Crystal Structure, and Electronic Spectrum of Ethylenediamineplatinum α-Pyridone Blue

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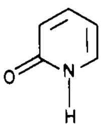
Interest in blue platinum species, known to form by oxidation of a variety of Pt(II) complexes with potentially bridging ligands, remains high.[1] Unfortunately, the paucity of pure samples and single crystals of these often oligomeric complexes leaves basic questions about their chemical nature unanswered. Despite extensive studies of their physical properties, the intriguing colors observed in solid samples of these materials are poorly understood. The only platinum blue that has previously been crystallized and characterized by X-ray diffraction is *cis*-diammineplatinum α-pyridone blue (**1**),[2] an amidate-bridged, mixed-valent, metal–metal-bonded Pt_4 complex with an average platinum oxidation state of 2.25. We now wish to describe the syntheses of two new crystalline platinum blues, the properties of which substantially enhance our understanding of this interesting class of compounds. Here we report the preparation, *x*-ray crystal structure, magnetic properties, and assignment of the visible spectroscopic bands of ethylenediamineplatinum α-pyridone blue ($[Pt_4(en)_4(C_5H_4NO)_4](NO_3)_5 \cdot H_2O$ (**2**)). In the accompanying paper[3] we describe the synthesis, properties, and crystal structure of *cis*-diammineplatinum 1-methyluracil blue (**3**), the first structurally characterized pyrimidine blue. Both the direction and relative magnitude of the shifts of the two principal absorption bands in **1–3** correlate with changes in the Pt–Pt distances and this result is discussed in terms of a model based on a recent SCF-Xα calculation for **1**.[4] The relationship between stereochemistry and electronic structure established here should prove valuable in understanding related platinum clusters.



α-pyridone, C_5H_5NO

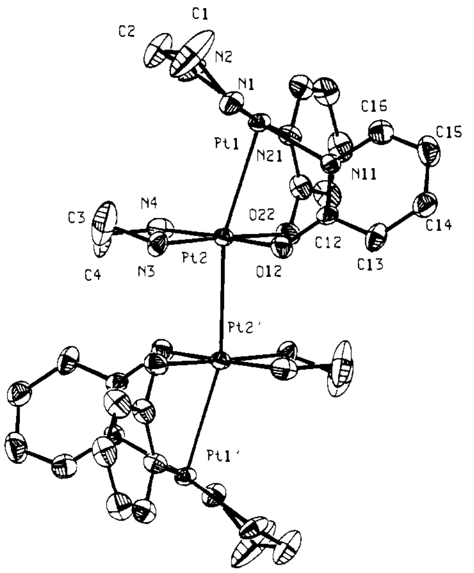


Figure 1. Structure of the $[Pt_4(en)_4(C_5H_4NO)_4]^{5+}$ cation (**2**) showing the 40% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms have been omitted for clarity. Selected interatomic distances: Pt1–Pt(2), 2.8296 (5); Pt2–Pt2, 2.9058 (6); ⟨Pt–N(en)⟩, 2.04 (1); ⟨Pt–N(α-pyridone)⟩, 2.04 (1); ⟨Pt–O⟩, 2.04 (1); Pt1–Pt2 twist angle ω = 24.3°, tilt angle τ = 32.1°.

Attempts to modify the synthetic procedure used for **1**[2b] failed to produce **2**, yielding only the known[5] head-to-head Pt(II) complex $[Pt_4(en)_4(C_5H_4NO)_4](NO_3)_4$ (**4**). It was possible, however, to oxidize 70 mg (43 μmol) of **4** dissolved in 15 mL of H_2O with 20 mg (21 μmol) of the binuclear Pt(III) head-to-head complex $[Pt_2(en)_2(C_5H_4NO)_2(NO_2)(NO_3)](NO_3)_2 \cdot 0.5H_2O$ (**5**),[6] in 1 mL of 3 M HNO_3, to obtain **2** and the head-to-head Pt(II) dimer $[Pt_2(en)_2(C_5H_4NO_2)]^{2+}$ (**6**) eq 1. After the nitric acid concentration of the resulting mixture was adjusted to 0.5 M, the blue solution was immediately frozen. Warming to 4 °C and filtration gave a blue powder in 40% yield which was recrystallized by dissolving in water at 0 °C and adjusting the HNO_3 concentration to 0.5 M to form **2**.[7]

$$\underset{\mathbf{4}}{2(Pt_4{}^{II})} + \underset{\mathbf{5}}{(Pt_2{}^{III})} \rightarrow \underset{\mathbf{2}}{2(Pt_3{}^{II}Pt^{III})} + \underset{\mathbf{6}}{(Pt_2{}^{II})} \qquad (1)$$

X-ray crystallographic study[8] showed **2** to be nearly isomorphous with **1**. The structure of the tetranuclear $[Pt_4(en)_4(C_5H_4NO)_4]^{5+}$ cation, displayed in Figure 1, is very similar to that of **1** except for the Pt(1)–Pt(2) and Pt(2)–Pt(2) distances. These have increased by 0.055 and 0.029 Å, respectively, due mainly to nonbonding steric interactions between ethylenediamine

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(7) Chemical anal. Calcd for $Pt_4C_{28}H_{50}N_{17}O_{20}$: C, 19.49; H, 2.92; N, 13.80. Found: C, 19.49, 19.39, H, 2.93, 2.88; N, 13.41, 13.39.

(8) Crystallographic analysis. The compound $[Pt_4(H_2NCH_2CH_2NH_2)_4(C_5H_4NO)_4](NO_3)_5 \cdot H_2O$ crystallizes in the triclinic system, space group $P\bar{1}$, with a = 10.652 (1) Å, b = 13.068 (2) Å, c = 9.413 (1) Å, α = 108.14 (2)°, β = 96.62 (1)°, γ = 68.39(1)°, V = 1157.7 Å^3, ρ_{obsd} = 2.485 (5) g cm^{-3}, ρ_{calcd} = 2.474 g cm^{-3}. By use of 2918 unique observed reflections collected with Mo K$\bar{\alpha}$ (λ 0.7107 Å) radiation out to 2θ = 50° on a CAD-4F single crystal diffractometer, the structure was solved and refined anisotropically to a current value of 0.030 for the discrepancy index R_1. Further work is in progress to locate and refine the position of the lattice water molecule suggested by the analytical data. Atomic and thermal parameters are provided as supplementary material.

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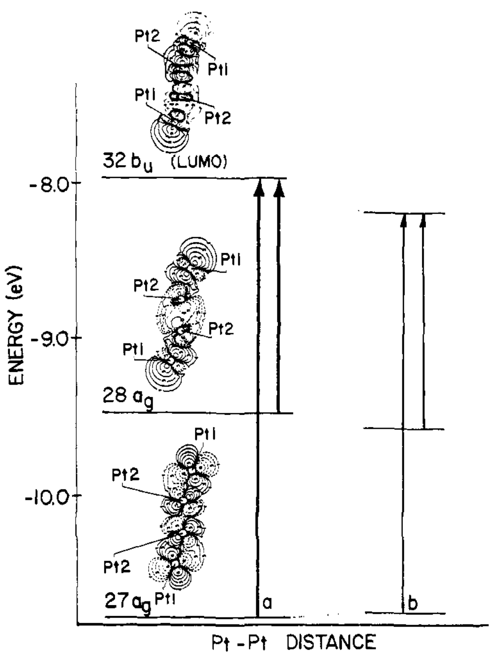

Figure 2. Effect of increasing the Pt–Pt distances on the energies of the molecular orbitals involved in the two main visible absorption bands in the α-pyridone platinum blues **1** (a) and **2** (b). The orbital contour plots depicted are adopted from those reported in ref 4.

rings in adjacent coordination planes (cf. the discussion in ref 5). The magnetic properties of **2** are also similar to those of **1**. A fit of the susceptibility data, measured on a SQUID susceptometer over the range $8\ K \leqslant T \leqslant 290\ K$, to the Curie–Weiss law gave an effective magnetic moment of 1.934 (3) μ_B per tetranuclear platinum unit. This value compares with that found for **1**, 1.81 μ_B,[2b] and is consistent with the presence of one unpaired electron per tetranuclear unit. Electron spin resonance spectra of solid samples of **2** are also nearly identical with those of **1**, confirming the presence of a mixed-valent $Pt_4^{2.25}$ cluster with delocalization of the unpaired spin over the four platinum atoms.

The visible spectrum of deep blue-violet solutions of **2** in 0.1 M HNO_3 has two principal absorption bands at 745 and 532 nm compared with values of 680 and 480 nm for **1**. These bands in **2** are shifted to lower energy by 0.159 and 0.252 eV, respectively, relative to **1**. Recent SCF–Xα calculations and single crystal polarized spectroscopic studies provided assignments for the optical transitions in **1**.[4] Using these results we have constructed a semiquantitative model of the corresponding transitions in **2**. The effect of increasing the Pt–Pt distances on the energy of the molecular orbitals involved in the visible transitions was deduced by inspection of the bonding character of the one-electron SCF-Xα wave functions of **1**, as shown graphically in Figure 2. The LUMO, 32 b_u, which is antibonding between all pairs of adjacent Pt atoms, is stabilized and moves to lower energy as the both inner and outer Pt–Pt distances increase. The antibonding Pt1–Pt2 interaction in 28 a_g, while weaker then the corresponding interaction in 32 b_u, is stabilized with increasing Pt1–Pt2 distance whereas the Pt2–Pt2 bonding interaction is destabilized as Pt2–Pt2 increases. Since there are two Pt1–Pt2 interactions for each Pt2–Pt2 interaction and since the Pt1–Pt2 distances are uniformly shorter than Pt2–Pt2, changes in the outer distances affect the energy of this orbital more than changes in the inner one. Thus 28 a_g shifts to lower energy, but not by as much as 32 b_u. The Pt–Pt interactions in 27 a_g are much weaker,[9] and a similar analysis suggests that the energy of this orbital will be increased slightly, if at all. This model (Figure 2) accurately accounts for the shift in both absorption bands of **2** and **3**[3] to lower energy, relative to those of **1**, and for the fact that the higher energy band shifts significantly more than the lower energy band.

In conclusion, the present study, together with the SCF–Xα results, establishes that the intense colors in the α-pyridone and 1-methyluracil platinum blues derive from intervalence metal-to-metal charge-transfer bands that vary predictably in energy with metal–metal distance. For other intensely colored platinum complexes, where the chromophore is tetranuclear with an average platinum oxidation state of 2.25, it is likely that color will correlate in a similar fashion with Pt–Pt distance. Thus green colors in analogues of **1** may indicate shorter Pt–Pt distances and purple colors may indicate longer ones, although more structural data are required before this correlation can be reliably extended. For clusters with higher average oxidation states[1h,10] analogous intervalence charge-transfer bands are to be expected.

Acknowledgment. This work was supported by PHS Grant CA 34992 awarded by the National Cancer Institute, DHHS. We thank Dr. W. H. Armstrong for assistance with the magnetic measurements and Engelhard Industries for a generous loan of K_2PtCl_4 from which the platinum compounds were synthesized.

Registry No. 2, 92127-09-8; **4**, 86372-66-9; **6**, 92127-11-2; Pt, 7440-06-4.

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

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(9) 70% of the electron density of 27 a_g is in the Pt1 spheres whereas 18% is in the Pt2 spheres.

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Characterization of a Platinum Pyrimidine Blue: Synthesis, Structure, and Physical Properties of *cis*-Diammineplatinum 1-Methyluracil Blue

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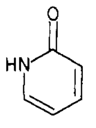
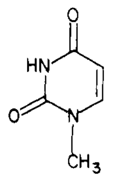
"Platinum pyrimidine blues" were first reported in 1975 as a class of blue platinum complexes with a high index of antitumor activity and low nephrotoxicity compared with the anticancer drug *cis*-diamminedichloroplatinum(II).[1] To date, however, no definitive structural information has been available for these paramagnetic blue compounds, despite extensive studies of their chemical and physical properties.[2,3] The presence of amidate-bridged, oligomeric species with partial metal–metal bonding and mixed oxidation states has been inferred for the platinum pyrimidine blues by analogy to the well-characterized, related compound *cis*-diammineplatinum α-pyridone blue (**1**).[4] In the pre-



α-pyridone



1-methyluracil
(1-MeUH)

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