J. Am. Chem. Soc. 1984, 106, 6428–6430

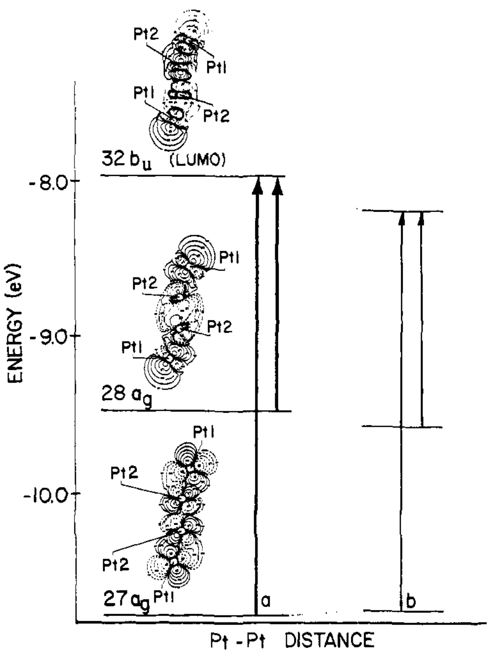

Figure 2. Effect of increasing the Pt–Pt distances on the energies of the molecular orbitals involved in the two main visible absorption bands in the α-pyridone platinum blues **1** (a) and **2** (b). The orbital contour plots depicted are adopted from those reported in ref 4.

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.

(10) Barton, J. K.; Rabinowitz, H. N.; Szalda, D. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 2827.

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

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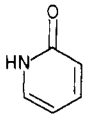
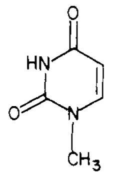
Received May 29, 1984

"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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(1) (a) Davidson, J. P.; Faber, P. J.; Fischer, R. G., Jr.; Mansy, S.; Peresie, H. J.; Rosenberg, B.; Van Camp, L. *Cancer Chemother. Rep., Part 1* **1975**, *59*, 287. (b) Speer, R. J.; Ridgeway, H.; Hall, L. M.; Stewart, D. O.; Howe, K. E.; Lieberman, D. Z.; Newman, A. D.; Hill, J. M. *Ibid.* **1975**, *59*, 629.

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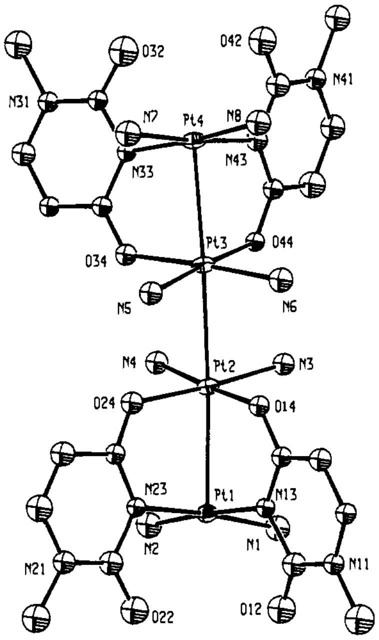

Figure 1. ORTEP drawing of *cis*-diammineplatinum 1-methyluracil blue (**3**) showing the atom labeling scheme and 40% probability thermal ellipsoids. All unlabeled atoms are carbon, and hydrogen atoms are omitted for clarity.

ceding paper[5] we describe the related ethylenediamineplatinum α-pyridone blue (**2**). We now report the highly reproducible synthesis, X-ray crystal structure determination, and magnetic and spectroscopic properties of *cis*-diammineplatinum 1-methyluracil blue ($[Pt_4(NH_3)_8(1\text{-}MeU)_4]^{5+}$ (**3**)). Brief mention of this compound, obtained with other products by treating the head-to-head (HH) dimer $[Pt_2(NH_3)_4(1\text{-}MeU)_2]^{2+}$ (**4**) with silver ion, was made previously, but no structural, magnetic, or UV-vis spectroscopic information was given.[3]

Compound **3** was prepared by allowing 1 mmol of *cis*-$[Pt(NH_3)_2(1\text{-}MeU)_2]\cdot 4H_2O$[6] to react with 1 mmol of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$[7] in 30 mL of water. The pH was adjusted to 5.5, and the solution was stirred at room temperature for 20 h. The resulting purple solution was acidified (pH ~1) with 7 N HNO_3, 1 g of $NaNO_3$ was added, and the solution was cooled at 0 °C for 3 h. A crop of ~80 mg of the nitrate salt of **4**[8] was collected by filtration. Addition of more (20 drops) 7 N HNO_3 and $NaNO_3$ (3 g) to the intense blue filtrate and standing at 0 °C gave dark blue needles of *cis*-diammineplatinum 1-methyluracil blue in 30% yield.[9] The perchlorate salt of **3** was also prepared (yield 35%) by using $AgClO_4$ and $HClO_4$ in place of $AgNO_3$ and HNO_3. Its optical and ESR spectral properties were almost identical with those of the nitrate salt.

The structure[10] of **3**, shown in Figure 1, consists of a tetranuclear unit of overall charge +5, corresponding to an average oxidation level of 2.25 per platinum atom. The geometry is similar to that found for the α-pyridone platinum blues **1** and **2**, except that the $Pt_4^{2.25}$ cation in **3** is not crystallographically required to be centrosymmetric. Two *cis*-diammineplatinum units are bridged in a head-to-head fashion by two 1-methyluracilate anions with deprotonated N3 and exocyclic O4 as the donor atoms. Two of these binuclear units are further associated through partial metal-metal bonding and NH···O hydrogen bonding across the central pair of platinum atoms in the $Pt_4^{2.25}$ cation. Other basic features of the structure, such as the canting of the coordination planes and the zig-zag chain [Pt(1)-Pt(2)-Pt(3) and Pt(2)-Pt(3)-Pt(4) angles, 165.0 (1)° and 164.8(1)°, respectively] are also retained. One minor difference is that, unlike **1** and **2**, in which the central pair of platinum-coordination planes are crystallographically required to be eclipsed, **3** has a twist angle of 22.3° about the Pt(2)-Pt(3) vector. Table I compares salient features of the structures of **1**, **2**, and **3**.

Table I. Comparison of Geometric Features and Optical Spectral Bands of Three Crystalline Platinum Blues

compd	Pt-Pt dist,[a] Å	Pt-Pt-Pt, deg	dihedral angle, deg[b] τ	dihedral angle, deg[b] ω	optical bands, nm	ref
1	2.774 (1)	164.6 (1)	27.4	22.8	480	4, 11
	2.877 (1)				680	
2	2.830 (1)	164.3 (1)	32.1	24.3	532	5
	2.906 (1)				745	
3	2.810 (1)	165.0 (1)	26.7	22.3	480	*c*
	2.865 (1)	164.8 (1)			520	
	2.793 (1)				740	

[a] For **1** and **2** the first distance reported is between the outer pair of platinum atoms and the second is between the inner pair; for **3**, the first and third distances are between the outer pairs of Pt atoms and the second is between the inner pair. [b] τ is the tilt angle between adjacent outer platinum coordination planes, and ω is the average torsion (or twist) angle about the outer Pt-Pt vectors in **1** and **2** and the inner such vector in **3**. [c] This work.

The magnetic susceptibility of a solid sample of the nitrate salt of **3** was measured on a SQUID susceptometer over the range $7 \leqslant T \leqslant 302$ K. A fit of the data to the Curie-Weiss law gave $\mu_{eff} = 1.89\ \mu_B$ per tetranuclear unit. This value compares favorably with those reported for **1** (1.81 μ_B[11]) and **2** (1.94 μ_B[5]) and confirms the presence of one unpaired electron per tetranuclear unit, as expected from the $Pt_4^{2.25}$ formulation. At liquid nitrogen temperature, powdered samples of both the nitrate and perchlorate salts of **3** exhibit axial ESR spectra ($g_\perp = 2.363$, $g_\parallel = 1.995$, $\langle g \rangle = 2.240$; from Curie constant, $\langle g \rangle = 2.19$) nearly identical with those of **1** and **2**. The ESR spectra of frozen (77 K) aqueous solutions of **3** reveal ^{195}Pt hyperfine-coupling interactions consistent with delocalization of the unpaired electron spin over all four platinum atoms in the chain.[11]

In 0.1 M HNO_3, **3** displays a moderately intense ($\epsilon \sim 1500\ M^{-1}\ cm^{-1}$) optical band at 740 nm, the position of which is identical with that of the uracil analogue.[12] The 1-methyluracil blue exhibits two weak absorptions ~520 and 480 nm, however, whereas the uracil blue (580 nm) and both **1** (480 nm) and **2** (532 nm) each have a single moderate absorption band. The relative positions of the visible absorption bands in **1**, **2**, and **3** correlate

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(4) (a) Barton, J. K.; Rabinowitz, H. N.; Szalda, D. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 2827. (b) Lippard, S. J. *Science (Washington, D.C.)* **1982**, *218*, 1075 and references cited therein.

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(9) Chemical anal. Calcd for $[Pt_4(NH_3)_8(1\text{-}MeU)_4](NO_3)_5\cdot 5H_2O$, $Pt_4C_{20}H_{54}N_{21}O_{28}$: C, 13.22; H, 3.00; N, 16.19; O, 24.65; Pt, 42.94. Found: C, 13.58; H, 2.99; N, 15.96; O (by difference), 24.56; Pt, 42.91. A sample that had been dehydrated by pumping in vacuo analyzed for $[Pt_4(NH_3)_8(1\text{-}MeU)_4](NO_3)_5\cdot 1.5H_2O$: Calcd for $Pt_4C_{20}H_{47}N_{21}O_{24.5}$: C, 13.69; H, 2.70; N, 16.77; O, 22.35; Pt, 44.49. Found: C, 13.65; H, 2.66; N, 16.41; O (by difference), 22.99; Pt, 44.29. The X-ray analysis[10] revealed a pentahydrate formula, in agreement with the above and an independent report.[3]

(10) X-ray analysis: The compound $[Pt_4(NH_3)_8(C_5H_5N_2O_2)_4](NO_3)_5\cdot 5H_2O$ crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 10.123$ (3) Å, $b = 13.084$ (4) Å, $c = 19.508$ (7) Å, $\alpha = 92.28$ (3)°, $\beta = 101.09$ (3)°, $\gamma = 107.49$ (2)°, $V = 2405.2$ Å^3, $\rho_{obsd} = 2.435$ (13) g cm^{-3}, $\rho_{calcd} = 2.430$ g cm^{-3}, $Z = 2$. By use of 2168 unique observed reflections collected with Mo Kα ($\lambda = 0.7107$ Å) radiation out to $2\theta = 40°$ on a single-crystal X-ray diffractometer, the structure was solved by standard Patterson and difference Fourier methods. Because of the very thin crystals and slow loss of water of crystallization, the data-to-parameter ratio was low (~6.7:1). The current value for the discrepancy index R_1 is 0.038. Atomic positional and thermal parameters are provided as supplementary material. Full details will be reported elsewhere.

(11) Barton, J. K.; Szalda, D. J.; Rabinowitz, H. N.; Waszczak, J. V.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 1434.

(12) Mascharak, P.; Lippard, S. J., unpublished results.

nicely with Pt-Pt distance (Table I), as predicted by a model[5] based on a SCF-Xα calculation[13] for *cis*-diammineplatinum α-pyridone blue.

In summary, a platinum pyrimidine blue has been structurally and magnetically characterized for the first time. The ability to prepare this species in pure cyrstalline form will facilitate further evaluation of this class of compounds as antitumor drugs. The geometric, magnetic, and spectroscopic properties of *cis*-diammineplatinum 1-methyluracil blue substantially extend the amplify our understanding of platinum blues as based on earlier studies of the α-pyridone analogue.

Acknowledgment. This work was supported by grants from the Bristol-Myers Co. and the National Cancer Institute under Research Grant CA-34992. We also thank Engelhard Industries for a loan of K_2PtCl_4, from which all platinum compounds were made, and W. H. Armstrong and T. V. O'Halloran for experimental assistance and helpful discussions.

Supplementary Material Available: Atomic positional and thermal parameters for compound 3 (2 pages). Ordering information is given on any current masthead page.

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Crystal Structures of Two Titanium Tartrate Asymmetric Epoxidation Catalysts

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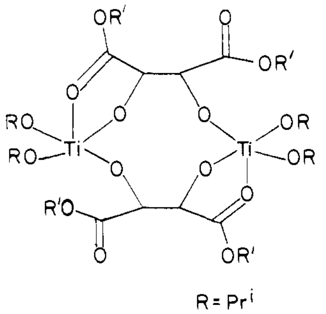
Received June 22, 1984

The enantioselective synthesis of organic compounds using chiral transition-metal complexes is an important, current topic in chemistry.[1] A recent contribution to this field has been the asymmetric epoxidation of allylic alcohols by alkyl hydroperoxides using titanium tartrate catalysts.[2] Previously, the structure of the binuclear titanium tartrate ester catalysts were presumed to be **1**,[3] on the basis of solid-state structural studies of binuclear vanadyl tartrate complexes.[4] Since the vanadyl structures were unsatisfactory models for several reasons, we have been trying to crystallize actual binuclear titanium tartrate catalysts for X-ray structural investigation. As described in the present communication, these efforts have been successful. Here we report the crystal and molecular structures of **2** and **3**, two catalytically active titanium tartrate complexes,[5] which should substantially aid mechanistic investigations of the asymmetric epoxidation reaction. To our knowledge, these are the first titanium "tartrate" structures to have been determined.



R = Pr^i
1 R' = Et, Pr^i

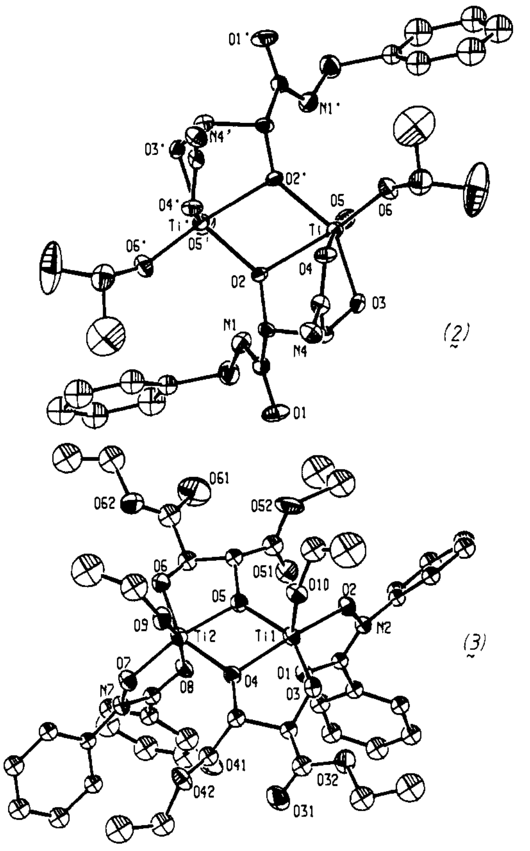
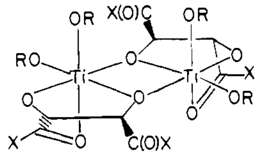
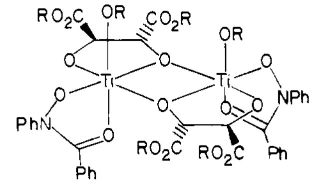


Figure 1. ORTEP drawings of **2** (top) and **3** (bottom) showing the atom labeling schemes and 40% probability thermal ellipsoids. For clarity, carbon atoms are not labeled and hydrogen atoms are omitted. In **2**, the benzyl groups on N4 and N4' and the isopropyl groups on O5 and O5' are also omitted for clarity.



R = Pr^i
2 X = NHCH$_2$Ph



3 R = Et

Compound **2** was synthesized by addition of 4.0 g (12.2 mmol) of (*R*,*R*)-*N*,*N*'-dibenzyltartramide to 80 mL of a stirring CH_2Cl_2 solution of Ti(O-*i*-Pr)$_4$ (3.64 g, 12.2 mmol). After 2.5 h the volatiles were removed in vacuo and the residue was dissolved in 30 mL of CH_2Cl_2. Removal of this solvent in vacuo[6] left a white foam, which was dissolved in 80 mL of ether with stirring. After 15 min, a white precipitate began to form at which point the reaction was placed in a −30 °C freezer. The precipitate was isolated by filtration, washed with 30 mL of ether, and dried in vacuo (yield, 61%). X-ray quality crystals were obtained from 8:1 toluene/CH_2Cl_2 over a 6-week period at −30 °C.[7,8] Compound

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(5) The catalytic activity of **2** is reported in: Lu, L. D.; Johnson, R. A.; Finn, M. G.; Sharpless, K. B. *J. Org. Chem.* **1984**, *49*, 728. The catalytic activity of **3** has been observed with α-phenylcinammyl alcohol (Ellman, J. A.; Pedersen, S. F., unpublished results).

(6) Dissolving the residue in additional solvent and then removing this solvent in vacuo helps remove most of the free alcohol released in the synthesis.