Chemical and Spectroscopic Characterization of *cis*-Diammineplatinum α-Pyridone Blue in Aqueous Solution. Comparison with Other Platinum Blues

Jacqueline K. Barton, Carl Caravana, and Stephen J. Lippard*

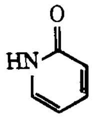
Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. *Received June 8, 1979*

Abstract: The spectral, redox, and chemical properties of *cis*-diammineplatinum α-pyridone blue (PPB), $[Pt_2(NH_3)_4(C_5H_4ON)_2]_2(NO_3)_5\cdot H_2O$, in aqueous solution have been studied and compared with those of other blue platinum complexes. The extinction coefficient of the blue chromophore is a sensitive function of the anions present and of the temperature. The approximately axial electron spin resonance spectrum is characterized by g values of 2.38 and 1.976, very similar to those reported from single-crystal ESR studies. Extensive ^{195}Pt hyperfine interactions indicate that PPB maintains its oligomeric structure upon initial dissolution in water. The decomposition of PPB in solution has been monitored by intensity losses with time in both the blue absorption band and the ESR signal. The concomitant decrease observed indicates the correspondence of the blue chromophore with the unpaired spin. Oxidative titrations of PPB show a linear decrease in A_{680} and ESR signal intensity with the addition of 3 equiv of ceric ion per tetramer. The chemical characteristics of PPB in solution are compared to those of platinum acetamide blue (PAB), *cis*-diammineplatinum uracil blue (PUB), and the newly characterized *cis*-diammineplatinum hypoxanthine green (PHG), the first reported platinum purine "blue". The results establish the similarity in their chemical composition and electronic structure. The electronic spectra exhibit broad absorption bands in the region 590–720 nm. These blue chromophores also depend upon the anions present. The ESR spectrum of PUB is strikingly similar to that of PPB, although of lower absolute signal intensity. This result may be due to spin-spin coupling since PUB is shown to be a longer chain oligomer. Both PHG and PAB exhibit a weak ESR transition. Oxidative titrations using ceric ion of PAB and PHG monitored spectrophotometrically show that 1.75 e^-/Pt is required for the complete loss of blue color; this result is consistent with oxidation to platinum(IV) from the initial platinum formal oxidation state of 2.25. Classical reductive titrations of the *cis*-diammineplatinum blues to platinum metal further support the oxidation-state assignment of 2.25. Gel electrophoresis of the *cis*-diammineplatinum blues, assuming the identical charge per monomeric unit, indicates the length of the oligomers to increase in the series PPB < PHG < PUB. These studies demonstrate that blue platinum complexes share the properties of mixed valency and oligomeric structure.

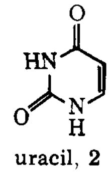
Although blue platinum compounds were reported in 1908,[1] the nature of these unusual materials remained elusive for many years. The original complex, termed "Platinblau", was isolated from the reaction of dichlorobis(acetonitrile)platinum(II) with silver salts. It was proposed[1] to be a platinum(II) monomer having the formula $[(CH_3CONH)_2Pt]\cdot H_2O$. During the reaction, acetonitrile had been hydrolyzed to acetamide. More recently, a trimethylacetamide platinum blue, formed in the reaction of $[(CH_3CN)_2PtCl_2]$ with trimethylacetamide, has been prepared and spectroscopically characterized.[2] This blue compound was formulated as the monomeric platinum(IV) species $[(Me_3CCONH)_2PtCl_2]$ and, by analogy, "Platinblau" was proposed to be $[(CH_3CONH)_2Pt(OH)_2]$. It has also been suggested that platinum acetamide blues are oligomeric with bridging acetamide ligands.[3] These structural proposals do not rationalize the distinctive blue chromophore, however.

A series of blue *cis*-diammineplatinum complexes having a variety of substituted pyrimidines as the amidate ligands is also known.[4] The realization that platinum blues possess a high index of antitumor activity with a lower associated nephrotoxicity than the parent drug, *cis*-$(NH_3)_2PtCl_2$, further stimulated efforts to characterize them.[4,5] Chemical,[6,7] spectroscopic,[8,9] magnetic,[6,8] and sedimentation[10] analyses of the unstable, amorphous platinum pyrimidine blues revealed them to be paramagnetic and oligomeric.

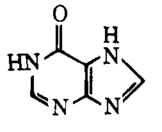
As described previously,[11,12] use of a pyrimidine analogue, α-pyridone (**1**), as the amidate ligand has enabled the synthesis of a crystalline platinum blue, the structure of which has been determined by X-ray diffraction. *cis*-Diammineplatinum α-pyridone blue (PPB) is comprised of a tetranuclear chain of platinum atoms linked through metal-metal bonding interactions, amidate bridges, and hydrogen bonds between ligand substituents. A schematic illustration of the structure is provided in Figure 1. The formal platinum oxidation state in this oligomer is 2.25, i.e., it is a mixed-valence complex. Chemical and crystallographic analyses are consistent with the formulation $[Pt_2(NH_3)_4(C_5H_4NO)_2]_2(NO_3)_5\cdot H_2O$. Magnetic susceptibility studies further support the assignment of one unpaired spin per tetramer. Single-crystal ESR studies indicate that the unpaired spin resides in a molecular orbital derived from atomic d_{z^2} orbitals directed along the platinum chain axis.[11b]



α-pyridone, **1**



uracil, **2**



hypoxanthine, **3**

The features of mixed valency, amidate bridges, and metal-metal bonded oligomerization found in the structure of PPB are quite likely shared by all of the aforementioned platinum blues. X-ray photoelectron spectra[13] of PPB, platinum uracil (**2**) blue (PUB), and the original platinum acetamide blue (PAB) reveal the similarity in their electronic structures. An EXAFS (extended X-ray absorption fine structure) study[14] of *cis*-diammineplatinum uridine blue shows it to have Pt-Pt distances comparable in length to those found in the structure of PPB. In order to examine more fully the chemistry of PPB and further compare it with other blue platinum species, the spectroscopic and redox properties of PPB and related blue platinum complexes in aqueous solution have been studied. The results of this work, reported here, enable comparisons to be made among PPB, *cis*-diammineplatinum uracil blue (PUB), the platinum acetamide blue (PAB), and a novel platinum purine complex, *cis*-diammineplatinum hypoxanthine (**3**) green (PHG).

Experimental Section

Preparation and Characterization of the Blue Platinum Complexes. The synthesis and analytical data for PPB, PUB, and PAB have been described previously.[11,13] Infrared spectral data are as follows.

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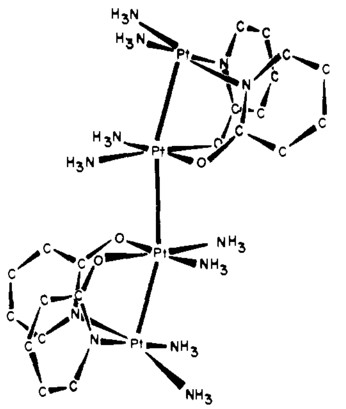

Figure 1. Schematic illustration of the structure of *cis*-diammineplatinum α-pyridone blue, but omitting hydrogen bonds. For further details, see ref 11b.

PPB in KBr Pellet: 3450 (br), 3130 (s), 2915 (sh), 2845 (sh), 1659 (sh), 1632 (sh), 1627 (sh), 1619 (sh), 1615 (s), 1600 (sh), 1569 (sh), 1552 (s), 1507 (sh), 1497 (sh), 1482 (s), 1440, 1388, 1357, 1184, 1160, 1125, 1039, 915 (w), 902 (w), 883 (s), 836, 802 (sh), 791 (s), 758 (w), 722 (w), 680, 633, 600, 532 cm^{-1}.

PUB in KBr Pellet: 3390 (br), 3190 (s), 2915 (sh), 2850 (sh), 1610 (br), 1517, 1478 (sh), 1446 (s), 1388, 1370, 1297, 1247 (w), 1220, 1184 (w), 1079, 1054, 1017 (sh), 990 (sh), 822, 801 (sh), 746, 699 (w), 612, 591, 560 cm^{-1}.

***cis*-Diammineplatinum Hypoxanthine Green (PHG).** Following the preparation of a 0.15 M solution of *cis*-diammineplatinum(II) hydrolysis products (1 mmol of platinum),[15] 0.136 g of hypoxanthine was dissolved in 12 mL of a warm (37 °C) aqueous solution at pH ≥10. This solution was quickly added to the platinum hydrolysis products and the pH adjusted to 5-7. The mixture was then immediately incubated at 37 °C in the dark so as to avoid the precipitation of hypoxanthine on cooling. After incubation for 1 day, the solution turned a turquoise blue-green in color. Incubation was halted after 3-5 days when no further deepening in color was observed. After filtration to remove any unreacted ligand, the green product was precipitated with an equal volume of ethanol and an excess of cold ether. Analyses for PHG yielded the following: (a) C, 11.4; H, 3.01; N, 19.6; O, 21.65; Pt, 44.2. (b) C, 10.63; H, 3.07; N, 20.67; O, 22.47; Pt, 42.2. These analyses reveal a platinum:hypoxanthine stoichiometry of greater than 1:1. Anal. Calcd for $Pt_5(C_5H_3N_4O)_4(NH_3)_{10}(NO_3)_{7.25}\cdot 5H_2O$: C, 10.79; H, 2.35; N, 20.92; O, 22.10; Pt, 43.82.

IR (PHG in KBr Pellet): 3410 (br), 3170 (br), 2960 (sh), 1764 (sh), 1738 (sh), 1728 (sh), 1715 (sh), 1682 (sh), 1640 (br), 1580 (sh), 1463, 1384 (s), 1356, 1260 (w), 1225 (w), 1182, 1117 (w), 1086 (w), 1038, 1020, 850 (w), 820 (s), 818 (sh), 770 cm^{-1}.

Attempts to Synthesize Other Purine Blues. Using the procedure employed in the synthesis of PHG, the preparation of other purine blues was attempted. The minimum volume necessary was used to dissolve completely the particular purine in warm, aqueous, basic solution. The formation of a blue (or green) product was not detected using any of the following purines: theobromine, theophylline, 6-methoxypurine, inosine, or guanosine.

Spectral Measurements. Infrared spectra were recorded using a Perkin-Elmer 621 or 137 spectrometer calibrated with polystyrene film. Atomic absorption analyses were conducted using a Varian-375 spectrometer with a carbon rod atomizer. Chemical analyses of platinum compounds were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Some platinum analyses were performed in our laboratory by atomic absorption spectroscopy, using standard solutions of K_2PtCl_4 as the calibrant. Electronic spectra were recorded on a Cary 118C spectrophotometer. In determinations of the decomposition of PPB with time, absorption spectra of an aqueous solution of PPB were taken at regular time intervals using a Cary repetitive scan attachment. Constant solution temperature was maintained using water-cooled jacketed cell holders. ESR spectra were obtained using a Varian E-line spectrometer. The microwave frequency was calibrated with diphenylpicrylhydrazyl. All ESR spectra were recorded at 77 K on frozen aqueous solutions using a Wilmad WG-816 ESR nitrogen Dewar. The decomposition of PPB in aqueous solution was monitored through ESR by incubating the sample tube in a constant-temperature bath for a given length of time, freezing in liquid nitrogen for the spectral measurement, followed by repeated incubation and freezing cycles. Since no changes were detected in the spectral intensities of frozen solutions over several days, only the incubation time at 20 °C was considered in the analysis of the decomposition kinetics.

Oxidative Titrations.[10] A solid sample of the blue platinum complex (~2 mg) was dissolved in 1 mL of 0.05 M HNO_3 and ammonium nitrate was added to a final concentration of 1 M. These salt conditions were found to minimize the instability of the blue platinum complexes in solution over the time interval required for the study. Aliquots (5-50 μL) of a stock (~0.015 M) ceric ammonium nitrate solution in 0.05 M HNO_3-1 M NH_4NO_3 were then added to the platinum solution. Platinum concentrations in the sample solution were determined either by weight or by atomic absorption spectroscopy. In spectrophotometric studies, aliquots of the ceric solution were added in a parallel fashion to the reference cell containing 0.05 M HNO_3. After each addition, spectra were recorded over the region 800-400 nm. No changes were observed in the spectra of the test solution between successive additions of ceric ion (5-10-min intervals). In the titrations of PPB monitored by ESR, 0.5-mL aliquots were repeatedly removed from the test solution to obtain spectra. The same quartz tube and instrument settings were used throughout the titration. Between additions of ceric ion, both the aliquot measured and the test solution were frozen in liquid nitrogen. After each measurement, the aliquot was returned to the test solution and additional ceric ion was added.

Reductive Titrations. The reduction of the blue platinum complexes to platinum metal was conducted by classical volumetric methods.[16] Permanganate solutions were boiled before use and standardized (2.5 × 10^{-3} M) against solutions of sodium oxalate. An excess of ferrous sulfate solution (6 × 10^{-4} M Fe(II) in 0.5 N H_2SO_4), previously standardized against the potassium permanganate, was added to the platinum solution prepared with a known weight of the platinum complex. The excess ferrous sulfate was then titrated using the standardized permanganate solution. Over the course of the titrations the solutions were colorless. End points were detected by the first stable appearance of pink color associated with an excess of permanganate ion; this small excess could then be back-titrated with ferrous sulfate solution. In the presence of α-pyridone, uracil, or hypoxanthine, the end point was difficult to discern; the pink color would slowly decay, leaving a colorless solution. These ligands were slowly oxidized by the permanganate ion; in the absence of these organic ligands, end points were sharp. Known quantities of the ligands were titrated using the potassium permanganate solution in order to correct for this ligand oxidation. Again, end points were only slowly discernible. These results were used to correct the data on the complexes; approximately 60% of the volume of the permanganate solution used oxidizes the ligands. Since this oxidative process is slow, solutions were left overnight (with excess permanganate), with stirring and nitrogen bubbling through them, to reach a stable end point.

Electrophoresis. Slab gel electrophoresis was used to estimate the relative lengths of the blue platinum oligomers. The slab gels were composed of 5% agarose in 0.2 M $NaNO_3$; the electrophoresis buffer was also 0.2 M $NaNO_3$. Aliquots (25 μL) of the blue platinum solutions (~0.02 M Pt) were mixed with an equal volume of 50% sucrose and thinly layered into the gel compartments. Electrophoresis was conducted for 4 h at 40 V using a Buchler 3-1500 power supply. Following electrophoresis, the individual channels of the agarose gels were sliced (7-mm wide columns) and then further sectioned longitudinally into 3-mm long segments. To each segment were added 100 μL of 30% peroxide and a trace quantity of ferrous sulfate to degrade the agarose. Samples were left to evaporate to dryness. This degradation procedure was then repeated. The product was subsequently dissolved in 0.5 mL of 0.1 N HNO_3 and platinum concentrations were determined by atomic absorption analysis. The atomization program used was 25 s/dry at 100 °C; 20 s/ash at 1300 °C; ramp at 600 °C/s; 1.5 s/atomize at 2300 °C. The absorbance at 265.9 nm was measured at least three times using 5-μL aliquots and the measurements were averaged.

Results

Synthesis. The *cis*-diammineplatinum blues were prepared using the general scheme shown in Figure 2. In this scheme the platinum hydrolysis product is written as *cis*-$[(NH_3)_2Pt(OH)(OH_2)]^+$, but is known to be a more complex

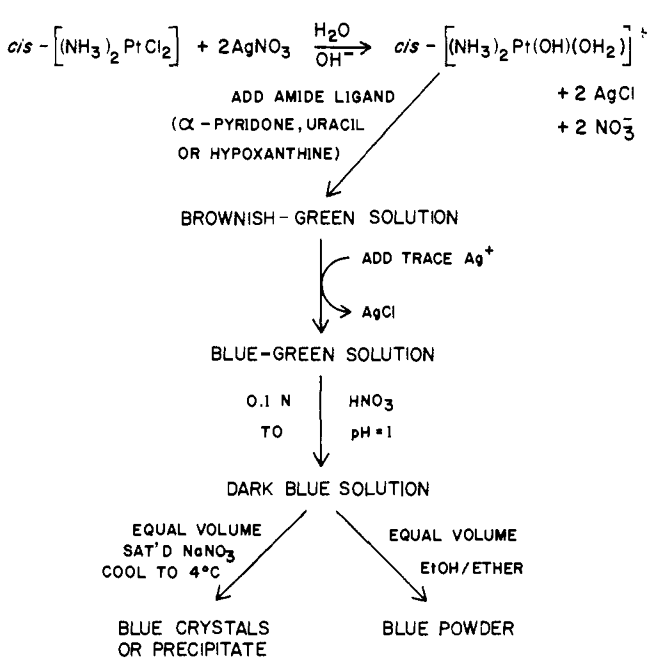

Figure 2. Preparative scheme used for *cis*-diammineplatinum blues.

mixture.[15] Only PPB was isolated reproducibly in pure crystalline form. Variations in the analytical data and visible spectra of other blues occurred with successive preparative batches. The kinetics of the reaction is pH dependent, relatively acidic conditions (pH 4-5) accelerating the rate. Incubation times varied from 1 to 5 days depending upon the initial pH value. The reaction also depends on the anions present. Addition of nitric acid following incubation dramatically intensifies the blue color. In the presence of a small amount of chloride ion, the incubation solution turns a brownish color rather than blue. This problem can frequently be remedied by precipitating the chloride with silver ion. Reports[4,6,7] that platinum blues cannot be prepared in the presence of acetic acid or chloride ion are perhaps accounted for by the discharge of the blue color in the presence of these ions. This discharge appears to be reversible, at least in the case of chloride ion. In addition, the spectral characteristics of isolated products were qualitatively observed to be a function of the concentration of reagents in the incubation mixture and the length of time incubated. When, in the synthesis of PUB, the platinum concentration was decreased through the range 0.2-0.07 M, a corresponding decrease by up to 30 nm was discerned in the band maximum of the higher energy one of the two visible transitions in the subsequently isolated PUB. Moreover, the extinction coefficient of both chromophores decreased by up to 80% in this series. The length of the incubation time is also a factor in determining the products formed. Variations in the band maximum and associated extinction coefficients of PPB, when isolated by ethanol/ether precipitation (Figure 2), and of PUB were observed for incubation times ranging from 1 to 14 days. Indeed, relatively long periods of incubation (>4 days) of PPB led only to the isolation of noncrystalline material. The spectral and chemical characteristics of these blue platinum pyridone powers, PPP, actually resemble more closely those of the purine and pyrimidine blues than those of the crystalline PPB (vide infra).

Spectral Properties and Chemical Reactivity of PPB. Electronic Spectrum. The visible spectrum of PPB, shown in Figure 3 as a function of time, is characterized by a broad transition centered at 680 nm. The inherent instability of this chromophore in solution as well as the unusual dependence of the absorption on experimental conditions leads to a large uncertainty in the extinction coefficient of this band. In aqueous solution at 25 °C (0 time), $\epsilon_{680}(\text{PPB}) = 60 \pm 15\ \text{M}^{-1}\ \text{cm}^{-1}$. Dilution of a prepared PPB solution variably decreases ϵ_{680}. In addition, the extinction coefficient of this band is a highly sensitive function of the anions present in solution. Nitrate or perchlorate salts increase ϵ_{680} by a factor of 5-20, while, in the presence of either chloride or acetate anions, the color is discharged completely. Similarly, nitric, perchloric, sulfuric, or hydrofluoric acids increase ϵ_{680} while hydrochloric or acetic acids decrease the extinction coefficient. The loss of blue color with the addition of chloride ion is, in fact, reversible. Following the addition of an equivalent amount of silver ion so as fully to precipitate AgCl, the blue color returns to within 95% of its original intensity. Moreover, the blue chromophore is qualitatively found to be temperature dependent. A decrease in temperature by 20 °C enhances the absorption by an order of magnitude. Concentrated solutions of PPB or solutions having an increased absorption as a result of anions present reveal an additional absorption band of lower relative intensity, centered at 480 nm. Nujol mull spectra of solid samples show a comparable transition. With the addition of nitric acid this band increases its intensity markedly relative to the transition centered at 680 nm (cf. Figure 3).

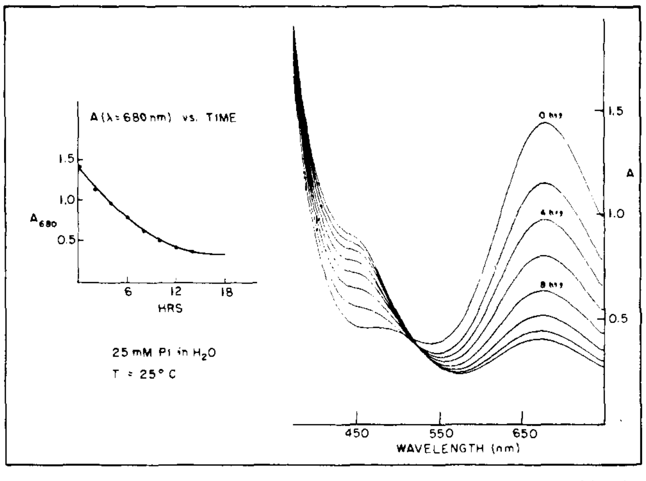

Figure 3. Visible spectrum of *cis*-diammineplatinum α-pyridone blue in aqueous solution as a function of time. The inset plots the decrease in A_{680} with time.

ESR Spectrum. In aqueous solution, the spectrum of PPB is characterized by a broad, approximately axial signal, $g_\perp \sim 2.4$ and $g_\parallel \sim 2.0$. Under conditions of moderate ionic strength, extensive hyperfine coupling interactions are resolved. The spectrum of PPB in 0.05 M HNO_3 is given in Figure 4. This spectrum can be described by the usual axial spin Hamiltonian

$$\mathcal{H} = \beta[g_\parallel S_z H_z + g_\perp (S_x H_x + S_y H_y)] + A_\parallel S_z I_z + A_\perp (S_x I_x + S_y I_y) \quad (1)$$

where β is the Bohr magneton, **S** is the effective spin operator ($S = 1/2$), **H** is the magnetic field, **A** is the hyperfine tensor, and I is the total nuclear angular momentum operator. In this axial spectrum, $g_\perp = 2.380$ and $g_\parallel = 1.976$. These values are identical with those determined by single-crystal methods,[11b] where $g_{xx}{}^2$ and $g_{yy}{}^2$ determined in the solid state have been averaged because in solution these perpendicular components cannot be independently resolved. In Table I are given the field positions and approximate intensities of hyperfine lines. In the perpendicular component of the spectrum, a regular signal pattern is observed where the peaks are separated by an average of 65 G. The high-field portion of this axial component shows at least four well-resolved hyperfine lines, while the low-field portion, showing only two peaks, is broadened and probably contains unresolved hyperfine structure. In the parallel component a

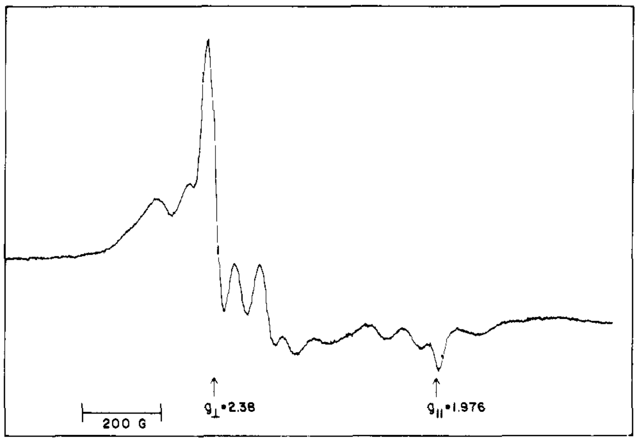

Figure 4. ESR spectrum of *cis*-diammineplatinum α-pyridone blue (5 mM Pt) in 0.05 M HNO_3. Microwave frequency = 9.132 GHz, modulation amplitude is 40 G. Microwave power is 14 mW. Receiver gain is 800. Time constant is 0.1 s.

Table I. Hyperfine Pattern in the ESR Spectrum of *cis*-Diammineplatinum α-Pyridone Blue[a]

Perpendicular Component				
peak max H_A, G	peak min H_B, G	$H_{1/2}$[b]	ΔH, G	% height[c]
2595	2631	2613	68	45
2676	2686	2681	65	55
2723	2769	2746[d]	63	100
2792	2826	2809	65	31
2858	2893	2876	58	30
2918	2950	2934	70	9
2990	3018	3004	66	3
3058	~3082	3070		0.5
Parallel Component				
H_A, G	H_B, G	$H_{1/2}$, G	ΔH, G	% height[c]
3134	3190	3162	80	28
3222	3264	3242	60	54
3290	3314	3302[e]	80	100
3360	~3406	3383		22

[a] Frozen, 0.05 M HNO_3 solutions were examined at 9.132 GHz. [b] $H_{1/2} = \frac{1}{2}(H_A + H_B)$. [c] Heights are relative to the central peak of each component. [d] $g_\perp = 2.376$. [e] $g_{\parallel} = 1.976$.

pattern asymmetric in terms of both intensity and field position is observed. This asymmetry is likely to be the result of second-order hyperfine interactions, given the large magnitude of the coupling.[17]

As has been reported previously,[11b] the measured g values are best described by a d_{z^2}-hole state, where **z** is taken along the mean Pt_4 chain axis, with admixtures of lower lying d_{xz}, d_{yz} states owing to spin-orbit coupling. The single-crystal ESR measurements have shown the orientation of $g_{\parallel}$ to be along the mean Pt_4 chain axis. We assign the hyperfine coupling to the interaction of the unpaired spin with ^{195}Pt nuclei. This isotope, having a 33.7% natural abundance, is the only naturally occurring platinum isotope having a nonzero nuclear moment, $I_{Pt} = \frac{1}{2}$. Assignment of the hyperfine splitting to ligand nuclei would be unreasonable given the small overlap of the d_{z^2} and ligand orbitals and the large magnitude of the coupling. Spectra of the one-dimensional solid-state platinum arrays, Pt(IV) doped Magnus' green salt[18] and irradiated K_2PtCl_4,[19] reveal comparable ^{195}Pt hyperfine coupling parameters and g values.

The extensive hyperfine coupling observed is consistent with the delocalization of the unpaired electron in PPB over a number of platinum centers. A localized unpaired spin would yield at most a three-line pattern from the superposition of transitions for $I_{Pt} = 0, \frac{1}{2}$. The calculated spectrum[20] for a platinum dimer having one delocalized unpaired spin also yields too few hyperfine lines to account for the pattern observed. The extensive ^{195}Pt hyperfine coupling in the spectrum of PPB, instead, supports at least a tetrameric structure for this mixed valent oligomer in solution. Analysis of this hyperfine pattern is made complicated owing to the statistical distribution of ^{195}Pt nuclei over the four platinum centers and, further, by the inequivalence of inner and outer platinum atoms in the tetrameric chain. If PPB were composed of isotopically pure ^{195}Pt and all platinum centers could be considered equivalent ($I_{tot} = 2$), a five-line pattern ($2I + 1$), following a binomial distribution, would be observed. The presence of a mixture of ^{195}Pt and spinless platinum isotopes would yield a nine-line pattern owing to the superposition of spectra from oligomers having I_{tot} equal to $\frac{1}{2}$, 1, $\frac{3}{2}$, and 2. In this case the intensity distribution, to first order, would be 0.2:4:23:68:100:68:23:4:0.2, where values are normalized to the intensity of the central peak. The poor resolution of the spectrum of PPB leads to an uncertain measure of the intensity distribution, X:X:X:45:55:100:31:30:9:3:0.5, where X denotes the unresolved signals at low field. For the parallel component, the measured values are 28:54:100:22. Despite the uncertainties, it is clear that the theoretical distribution given above does not correspond to the measured intensities. This analysis has not, however, included effects due to the inequivalence of platinum centers. Taking this inequivalence into account, and assuming the hyperfine coupling of platinum atoms at the chain ends to be twice that of the inner platinum atoms, $a_{outer} \sim 2a_{inner}$, a theoretical distribution was calculated as 0.3:3:8:22:48:62:100:62:48:22:8:3:0.3. This difference in hyperfine coupling constant would reflect an equivalent difference in the unpaired electron density between the inner and outer metal atoms.[21] The integral relationship between a_{inner} and a_{outer} has been invoked because of the regularity in the pattern observed. Details are given in ref 20. While the fit is still poor, deviations in the spectral amplitudes may be a function of resolution, line broadening, and second-order corrections which have been neglected in this analysis; second-order splitting would lower intensities of the high-field portion of each component. The examination of the spectrum of an isotopically pure ^{195}Pt α-pyridone blue would probably clarify the basis for the intensity distributions.

Double integration of the PPB spectrum (Figure 4) shows the signal to correspond to 0.8 ± 0.2 unpaired spins/tetramer relative to standard solutions of an EDTA-Cu(II) complex. Although large intensity increases in the blue chromophore have been noticed in the presence of a variety of anions, comparable effects were not observed in the ESR spectral intensity. On the other hand, a reduction in unpaired spin intensity has been quantitatively measured with successive additions of chloride ion. Titration with 0.8 equiv of chloride ion per tetramer eliminates the solution paramagnetism. This finding parallels the reversible loss of blue color in chloride containing PPB solutions. Chloride anions may coordinate axially to the platinum chain and serve to bridge the oligomers. Nitrate anions are only loosely associated with both ends of the platinum tetramer in the solid state.[11] Axial bridging of the paramagnetic complexes by chloride ion could lead to the pairing of spins and, consequently, to the loss of the blue color.

Decomposition of PPB in Solution. The diminution with time at 25 °C in both the blue absorption band (Figure 3) and the ESR signal intensity shows that PPB decomposes slowly in solution. As can be seen in Figure 5, the decrease in A_{680} with time parallels that found in the ESR signal intensity. Both the blue color and unpaired spin intensity are reduced at the same rate. This finding demonstrates the correspondence of the blue chromophore with the unpaired spin in this mixed valent tetramer.

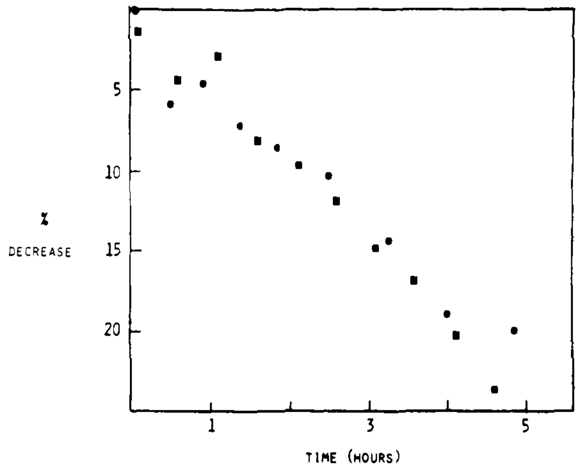

Figure 5. Decomposition of *cis*-diammineplatinum α-pyridone blue (13 mM Pt) in aqueous solution at 25 °C, followed by observing the percent decrease with time in ESR height of $g_\perp$ (●) and the visible absorption at 680 nm (■).

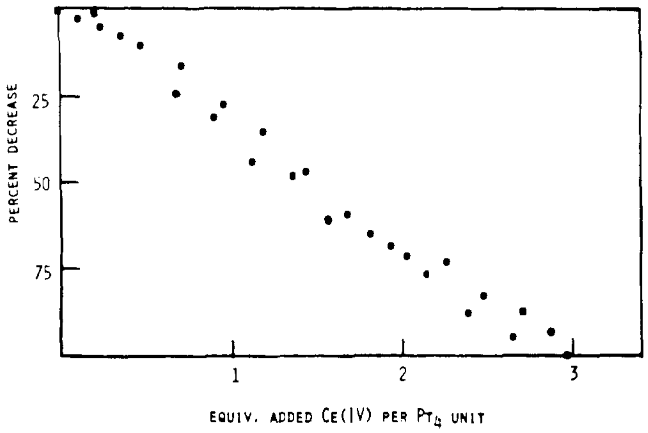

Figure 6. Oxidative titrations of *cis*-diammineplatinum α-pyridone blue (2.6 mM Pt) with cerium(IV) in 0.05 M HNO_3, monitored by the percent decrease in ESR height of $g_\perp$ (●) and the visible absorption at 680 nm (■). Solid ammonium nitrate (1 M final concentration) was added to stabilize the platinum complex over the course of the experiment.

The decomposition of PPB as measured spectrophotometrically depends upon pH, concentration, and the presence of anions. High ionic strength increases the rate of decay of the blue chromophore. The addition of base, pH ≥ 8, results in an abrupt loss of the 680-nm absorption that cannot be reversed with the subsequent addition of acid. Acidic media (pH ≤ 2) lower the decay rate relative to neutral pH at comparable solution ionic strengths. The presence or absence of oxygen does not affect the rate of decomposition. Solid ammonium nitrate in solutions of PPB stabilizes the chromophore for periods as long as 4 h. At ambient temperatures, however, no conditions have been observed that stabilize solutions of the complex indefinitely.

Oxidative Titration of PPB. The oxidation of PPB by Ce(IV) has also been monitored both spectrophotometrically and by ESR. Figure 6 displays the linear decrease in percent intensities of both A_{680} and the $g_\perp$ ESR transition with the addition of 3.08 equiv of ceric ion per tetramer. The blue absorption band decreases in intensity without a shift in its band maximum. The band centered at 480 nm likewise shows a reduction in intensity, although an initial increase in absorption has been observed; no correlation between this initial enhanced absorption and equivalents of added cerium was noted. The ESR spectrum, characterized by extensive hyperfine interactions under these ionic strength conditions, shows a similar linear reduction in intensity. Concomitantly, a new weaker signal at high field, $g = 2.06$, grows in, increasing to a plateau with the addition of 3 equiv of Ce(IV)/tetramer. This same signal appears in solutions containing tetrachloroplatinate oxidized by ceric ion and is therefore assigned to cerium(III).[22]

The linear decrease in unpaired spin intensity and blue color with the addition of 3 equiv of oxidant per tetramer reveals some important features of PPB in solution. Firstly, the end-point value of 0.77 equiv of oxidant per platinum atom demonstrates that PPB initially maintains an oligomeric structure in solution. A tetranuclear structure, or some multiple thereof, is necessary to account for oxidation by an integral number of electrons. Secondly, this titration again reveals the parallel behavior of the unpaired spin intensity and the blue chromophore. As the blue color is titrated, the unpaired spin intensity decreases. Thirdly, this linear decrease in unpaired spin intensity with the addition of 3 equiv of oxidant per tetramer indicates that PPB undergoes a multielectron oxidation. Alternative schemes may be ruled out for the following reasons. Upon addition of 1 equiv of oxidant, the ESR signal intensity neither increases nor decreases completely to zero, as would be expected if a tetranuclear intermediate having an average platinum oxidation state of 2.5 were formed or if the complex decomposed to $[Pt(II)]_2$ and $[Pt(III)]_2$ dimers. Successive additions of ceric ion also do not lead to an increase in intensity followed by a decrease, paralleling the formation and oxidation of new paramagnetic platinum oligomers, nor to any new ESR signals other than one readily ascribed to Ce(III). The data are therefore consistent only with a multielectron oxidation. The oxidative decomposition is likely to be irreversible, given the strictly linear dependence of the unpaired spin intensity on the equivalents of cerium added. The irreversibility of the multielectron oxidation has been observed in a preliminary electrochemical study.[23] Potentiometric titrations[24] of PPB in 4.5 N HCl also reveal an end point in the ceric ion oxidation at 3 equiv. Oxidation of PPB to form two diamagnetic platinum(III) dimers would nicely account for these data. No attempt was made to isolate such a species, however.

Other Blue Platinum Complexes. Spectral Properties. Table II summarizes the spectral characteristics of various *cis*-diammineplatinum blues. While the crystalline PPB shows a reproducible chromophore centered at 680 nm, powders isolated following long-time incubations (PPP) show variations in band maxima and extinction coefficient. PUB exhibits the greatest variation in its absorption spectrum, with band maxima reported to be centered at 730 and 590, ~620 and ~560, or 680 nm.[6] PHG shows variations over a much smaller range with the maximum at 710-730 nm. Unlike PPB and PUB, which are characterized by broad bands (~150 nm width at half-height), the spectrum of PHG reveals narrow bandwidths (50 nm width at half-height). These transitions have associated extinction coefficients that again vary with preparation over the range 70-400 M_{Pt}^{-1} cm^{-1}. The crystalline PPB has the lowest extinction coefficient in this series. These extinction coefficients vary with anions present, decreasing in the presence of chloride or acetate and increasing with nitrate or sulfate. The magnitudes of these changes, however, are substantially reduced relative to crystalline PPB; ϵ_{PUB} varies by a factor of 2-5 while ϵ_{PHG} increases only by 30-50% and shows only a 10% decrease with addition of chloride ion. These compounds also decompose in solution, as determined spectrophotometrically, but again to a lesser extent than does PPB, and dependent upon the preparation. It therefore appears that solutions of these complexes are similar in kind to those of PPB but differ somewhat in the degree of their instability.

The electronic spectra of the platinum acetamide blues (PAB) have been examined previously.[2] A broad absorption band is centered at 600-680 nm. Most notable in comparison

Table II. Characteristics of *cis*-Diammineplatinum Blues

compd	amide	λ_{max},[a] nm	ϵ,[a] M_{Pt}^{-1} cm^{-1}	ESR	platinum oxidn state[b]
PPB (PPP)	**1**	680, 480 (720, 590 610-630)	60, 20 (100-400, 30-50 100-400)	$g = 1.975$, $a_{\parallel} \sim 100$ G $g_{\perp} = 2.38$, $a_{\perp} = 65$ G	2.27 ± 0.10
PUB	**2**	730, 590 680 610-630, 550-570	100, 40 400 100-300	$g_{\parallel} = 1.97$, $a_{\parallel} = 110$ G $g_{\perp} = 2.38$, $a_{\perp} = 66$ G	2.08 ± 0.15
PHG	**3**	730, 710, 590	200-250, 200-230, 60-85	$g = 1.98$	2.28 ± 0.17

[a] The differing values represent a series of different batches. [b] By reductive titration. [c] Values in parentheses refer to various noncrystalline preparations of the α-pyridone powder.

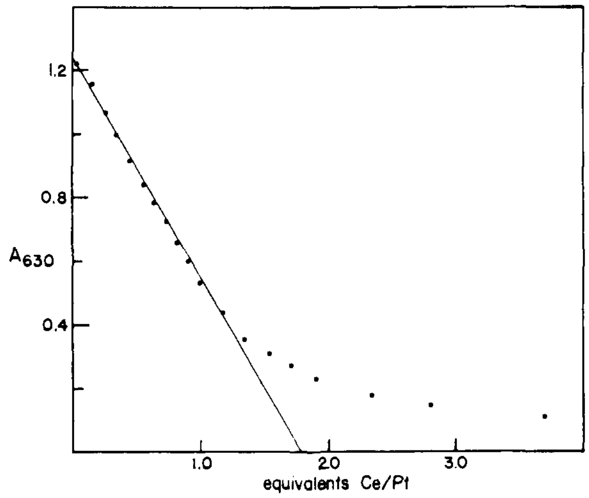

Figure 7. Oxidative titration of platinum acetamide blue (0.9 mM Pt) monitored spectrophotometrically.

to the *cis*-diammineplatinum blues is the magnitude of the extinction coefficient of this transition, ϵ 1100–1500 M_{Pt}^{-1} cm^{-1}. Like the *cis*-diammineplatinum blues, acids and salts affect this extinction coefficient following the removal of chloride ion.

The ESR spectral parameters of the *cis*-diammineplatinum blues are also given in Table II. The spectrum of PUB[8] is strikingly similar to that of PPB, indicating the similarity in their structures. As with PPB, extensive ^{195}Pt hyperfine interactions are observed. The intensity distribution in the perpendicular component is difficult to resolve but resembles that of PPB. The intensity of this signal, however, is substantially lower than that of PPB. While the ESR parameters do not vary with preparation, it appears qualitatively that the relative intensities do vary. Reaction mixtures of PHG and PAB show very weak ESR signals, with g(PHG) = 1.98 and g(PAB) = 2.05. Only these solutions were of sufficient concentrations to obtain signals. The weakened ESR spectral intensities of these oligomers could be the result of long-range spin-pairing effects.

Oxidative Titrations. The oxidation of PHG and PAB by ceric ion has also been monitored spectrophotometrically. Figure 7 shows the results for the oxidative titration of PAB. As can be seen by comparison to Figure 6, PAB undergoes a different oxidative reaction than does PPB. While the blue absorbtion band of PPB decreases linearly with the addition of 0.75 equiv of cerium/platinum, the blue chromophore here decreases with the addition of 1.75 equiv of cerium/platinum. The end point of 1.77 is obtained by linear extrapolation to the ordinate intercept in the plot shown. The nonlinearity at high cerium/platinum ratios indicates that the reaction is not quantitative.

In the case of PHG, results similar to those found with PAB have been obtained. Calculations based on several experiments reveal an end-point value of 1.54 ± 0.20 equiv Ce/Pt. Deviations from linearity are seen at high cerium/platinum ratios. The oxidation of PUB could not be measured by this procedure since precipitation occurred with successive additions of ceric ion.

The foregoing results show that the metal oxidation state is nonintegral in these blue platinum complexes as well. Assuming an initial formal oxidation state of 2.25, the removal of 1.75 electrons/platinum produces platinum(IV) end products. Platinum species having a tetravalent formal oxidation state are chemically reasonable products of this oxidation; oxidation of tetrachloroplatinate(II) by ceric ion similarly yields platinum(IV) species.[10]

Reduction of Blue Platinum Complexes. The formal metal oxidation state in these blue platinum complexes has also been examined by reductive titrations[16] of the compounds to platinum metal. The results of several redox titrations are also shown in Table II. Different preparations of the blue platinum complexes were assayed by this procedure. The deviations observed may be a function of compositional variations within these batches and of experimental error. Despite the large deviations, these analyses do support a mixed valent formulation of the *cis*-diammineplatinum blue complexes.

Gel Electrophoresis. In an effort to determine the relative sizes of the *cis*-diammineplatinum blue complexes, gel electrophoresis studies were carried out. The relative mobilities of the blues were monitored both visually and by atomic absorption analyses for platinum. Owing to the solution density (25% sucrose) and high percentage (5%) of agarose used, the deeply colored solutions entered the gel as sharp bands. These bands became increasingly more diffuse as the complexes migrated through the gel. When the blue-colored PPB solution entered the gel, the color changed abruptly to yellow. No color change was found in the case of PUB or PHG. This difference is not surprising, given the sensitivity of the blue chromophore in PPB to experimental conditions. It cannot be stated that no structural perturbations of these blue complexes have occurred during electrophoresis, however.

The migration patterns of these complexes in a typical electrophoresis experiment are shown in Figure 8. Platinum concentrations as a function of distance migrated were determined by atomic absorption analysis of degraded gel slices. The ordinate of the plot represents the atomic absorption of a particular complex and therefore its platinum concentration, normalized to the maximum absorption of that species along the gel. The patterns are characterized by very broad bands with maxima for this gel centered at 31, 41, and 49 mm for PUB, PHG, and PPB, respectively.

Assuming the chemical formulation of the blue *cis*-diammineplatinum complex monomeric repeat unit to be $[(NH_3)_2Pt(amidate)]^{1.25+}$, the relative gel electrophoretic mobilities of these cations should reflect their differing molecular weights. That these complexes carry approximately the same electrostatic charge per monomeric unit is supported by the chemical and redox analyses. The low chemical analysis for hypoxanthine in PHG should be recalled in this context, however. Substitution of this anionic ligand by a neutral ligand, e.g., water, would lead to an increase in positive charge of the complex and an artificially small value for its relative size. This assay then gives a minimum relative length for PHG. Platinum acetamide blues, having a stoichiometry of two amides per platinum in the monomeric unit, cannot be examined comparatively by this procedure because the electrostatic charge per monomeric unit is less positive than that of the *cis*-diammineplatinum blues. The relative mobilities of the *cis*-diammineplatinum blues show their relative sizes to increase in the series PPB < PHG < PUB. The breadth of the bands, moreover, reflects a large size distribution in these linear platinum oligomers. In analogous experiments where the α-pyridone powder was included, its relative size was reproducibly found to be greater than that of the crystalline tetramer, as one would expect. Its size relative to other blues, however, varied with different preparative batches.

Discussion

Solution Properties of *cis*-Diammineplatinum α-Pyridone Blue. The spectroscopic evidence and redox characteristics presented here demonstrate that PPB maintains a mixed valent oligomeric structure upon initially dissolving in aqueous solutions. The ESR spectral results, showing one unpaired electron per tetramer and extensive ^{195}Pt hyperfine interactions, are consistent with magnetic susceptibility data of solid samples and chemical and crystallographic analyses that reveal the chemical formulation to be $[Pt_2(NH_3)_4(C_5H_4NO)_2]_2^{5+}$.[11] The visible spectrum is characterized by a broad transition centered at 680 nm. The close correspondence between this characteristic absorption and the mixed valent character of the complex is apparent from studies monitoring changes in both the ESR signal intensity and this absorption band. As the oligomer decomposes in solution, the visible absorption and unpaired spin intensity decrease concomitantly. Oxidative titrations of PPB to form diamagnetic products also reveal a parallel reduction in the ESR signal and intensity of the blue chromophore. The oxidative titration with ceric ion further supports the conclusion that, initially, solutions of PPB contain the tetranuclear structure determined in the solid state. To effect a complete reduction in absorption intensities, 0.75 equiv of ceric ion is required per platinum atom. If, in solution, PPB were rapidly to decompose, for example, into $[Pt^{II}]_2$ and $[Pt^{II}Pt^{III}]$ dimers, oxidation of the platinum(II) dimer would lead to increases in the intensity of color and unpaired spin density. In addition, shifts in band maxima associated with these transitions might be expected. The formulation of a tetrameric PPB solution structure, or some integral multiple thereof, is required to avoid proposing species having fractional electron occupancies.

PPB does decompose in solution and this decomposition probably involves degradation of the oligomer into smaller, diamagnetic products. The stabilization of the blue chromophore for short time intervals with ammonium ion suggests that the ammine ligands may become labilized in the degradative process. Chemical analyses of *cis*-diammineplatinum blues show variably low values for the nitrogen content.[10,11] Indeed, a purple cyclopropylamineplatinum 1-methylthymine compound, prepared by analogous methods to that used for PUB, has a chemical analysis consistent with a stoichiometry of only one amine ligand per platinum atom.[10] In addition to steric considerations, coordination of a heterocyclic nitrogen atom trans to the ammine may influence this lability.

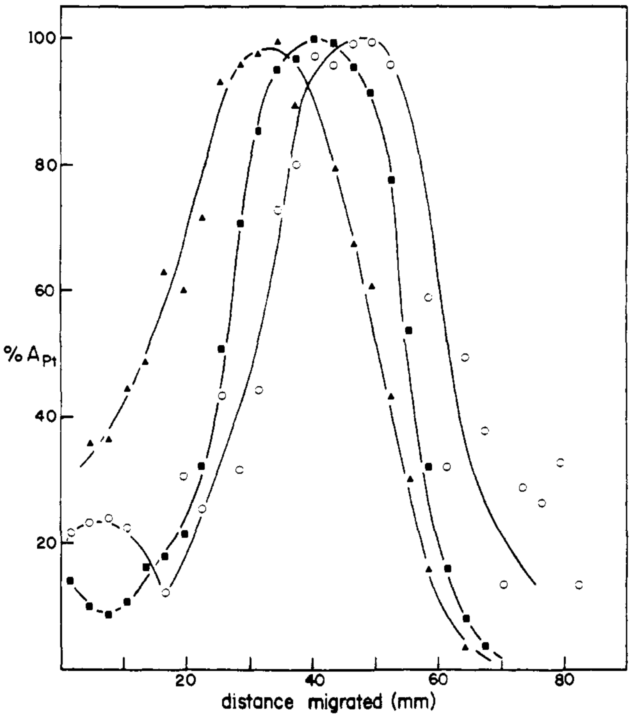

Figure 8. Electrophoresis of (▲) PUB, (■) PHG, and (○) PPB in 5% agarose gels. Following electrophoresis, gels were sliced, degraded, and assayed by atomic absorption. The ordinate represents the platinum atomic absorbance of each fraction relative to the maximum absorbance along the gel.

Common Characteristics of Blue Platinum Complexes. The similarity in chemical and spectroscopic characteristics of the various blue platinum complexes examined strongly suggests that the features of mixed valency, oligomerization, and amidate bridging are shared by them all in solution. Platinum blues are characterized by a broad transition in the visible region in the range 550–730 nm. The extinction coefficient of this transition shows an unusual sensitivity to experimental conditions. The most dramatic changes are found in solutions containing PPB. An ESR signal has been observed in frozen solutions of all the blue platinum compounds investigated, although the paramagnetism is substantially diminished in comparison to solutions containing PPB. Except for its lower intensity, the ESR spectrum of PUB is remarkably similar to that of PPB. Both the magnitude of the *g* values and hyperfine coupling parameters of PPB and PUB closely resemble one another. ESR spectra from solutions of δ-valerolactam blue have also been reported[8] and these appear to be identical with those of PPB and PUB. This characteristic spectrum indicates that PUB and the δ-valerolactam blue, like PPB, are paramagnetic and oligomeric. The ^{195}Pt hyperfine coupling interactions reveal electron delocalization over several platinum atoms. The very low intensity of the ESR signals found in PAB and PHG does not permit the resolution of comparable transitions.

The mixed valent character of blue platinum complexes has further been demonstrated in redox titrations. Reductive titrations of *cis*-diammineplatinum blues to platinum metal are consistent with the assignment of nonintegral oxidation states. Spectrophotometric titrations of PAB and PHG with ceric ion as the oxidant indicate that 1.75 equiv of Ce(IV) per platinum atom is necessary for complete oxidation. Assuming the products of this oxidation to be platinum(IV) species, a formal platinum oxidation state assignment of 2.25 must be inferred

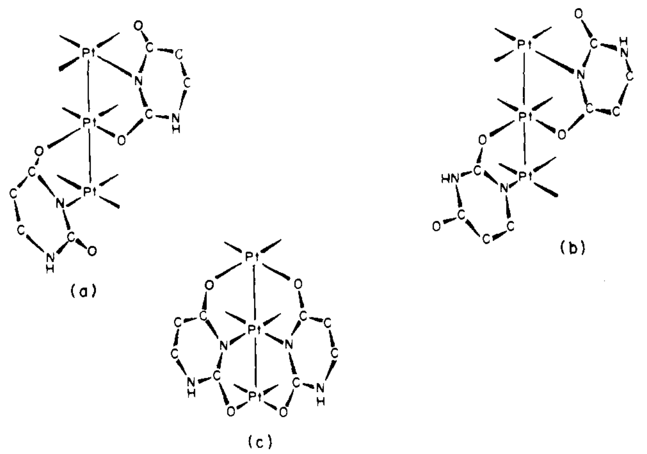

Figure 9. Possible structures for platinum uracil blue having (a) alternate singly bridging uracil anions; (b) a mixture of amidate linkages through both deprotonated N1 and N3 nitrogen atoms of uracil; (c) three platinum atoms bridged by two uracil anions through N3 nitrogen atoms and both exocyclic oxygen atoms, O2 and O4 (reproduced by permission from ref 12).

for the blue platinum reagents. Spectrophotometric titrations[10] of cyclopropylamineplatinum 1-methylthymine purple using ceric ion have, analogously, shown these purple platinum complexes to be mixed valent. In this instance, a platinum oxidation state of 3.75 was assigned on the basis of the oxidative titration. There is an interesting difference between these "blue" platinum complexes and the α-pyridone blue. While PAB and PHG are oxidized directly to platinum(IV) species, PPB is oxidized instead to an intermediate platinum(III) complex (see also ref 24). Perhaps the oligomeric structure of PPB with two bridging α-pyridonate ligands (Figure 1) facilitates oxidation to platinum(III) dimers. A structure similar to that of the sulfate bridged dimer[25] $[Pt_2(SO_4)_4]^{2-}$ seems likely. A more complex polymeric structure, with single bridging amidate ligands (Figure 9a) might not facilitate the formation of stable platinum(III) bridged dimers.

Gel electrophoresis provides a qualitative assay for the relative lengths of the *cis*-diammineplatinum blues. Assuming identical positive charges per monomeric unit, the mobility of these linear chain complexes in a gel correlates inversely with their relative lengths. The migration of a long polymer is restricted by the gel matrix relative to that of a shorter oligomer. Electrophoresis studies show the relative lengths of these complexes to increase in the series PPB < PHG < PUB. It is therefore not surprising that only the smallest oligomer, PPB, has been crystallized thus far. Samples of the α-pyridone powder, a noncrystalline material obtained following long-term incubation of reagents used to prepare PPB, consistently exhibited mobilities lower than that of PPB. Estimates based on sedimentation[10,26] as well as mass spectral[9] analyses suggest that PUB is composed of a distribution of oligomers with a size averaging 20 platinum units in length. The *cis*-diammineplatinum blues are valuable electron microscopic stains and bind strongly and cooperatively to polyanionic DNA, presumably because they are long, cationic polymers.[27]

Platinum chains could be propagated through an extensive arrangement of amidate bridges and hydrogen bonds between ligand substituents, as well as metal-metal bonds, such as those found in PPB. The polymeric uracil blue could be extended using alternate single bridged uracilate anions rather than through doubly bridged species found in the structures of PPB and the *cis*-diammineplatinum 1-methylthyminate dimer.[28] It is this double bridged arrangement that precludes further oligomerization of PPB owing to the steric factors imposed by the α-pyridonate ring.[11] Some proposals for the structure of PUB are given in Figure 9. Uracil offers two distinct sites for bridged metal coordination, N1 and O2, or N3 and O4. PUB may contain a mixture of these coordinating units. Uracil also contains hydrogen bond acceptors available for bonding to ammine ligands of adjacent units. In the structure of PPB the central metal-metal bond is reinforced by four hydrogen bonds between the pyridonate oxygen atoms of one dimer and the ammine ligands of the neighboring dimer.

The several unsuccessful attempts to synthesize blue complexes using other alkylated purine ligands suggests that hypoxanthine (**3**) bridges platinum centers through the deprotonated N1 nitrogen and O6 oxygen atoms in PHG. Both theophylline and 6-methoxypurine, with available coordination sites respectively at N7-O6 and N1-N9, although sufficiently water soluble, cannot be employed in the synthesis of blue platinum complexes. The failure in preparing blue complexes using inosine or theobromine is likely to be a function of their low water solubility; high reagent concentrations are required to oligomerize the *cis*-diammineplatinum(II) units. Stereochemical considerations may also be a factor in preventing the formation of blue complexes with guanosine. In this instance the exocyclic amine substituent at C2 may interfere with further oligomerization; in a structure analogous to that of PPB using guanosine, this amine substituent would be directed toward the platinum chain, inhibiting for steric reasons further oligomerization in that direction. The formation of dimeric units bridged by guanine is not precluded, however.

The variations in the lengths of the blue platinum oligomers may account for the differing observed spectral properties and rates of decomposition. For example, the smallest oligomer, PPB, shows the greatest instability in solution. The size of the oligomer may also affect the intensity of the ESR transition. The paramagnetism in long platinum chains could be diminished owing to the pairing of spins through a delocalized molecular orbital framework. Only PPB exhibits an unpaired spin intensity consistent with its mixed valent formulation. The α-pyridone powder, in contrast, shows a marked reduction in paramagnetism as do the other blue oligomers. Different preparative batches of blue platinum compounds, isolated under seemingly identical conditions, yielded products differing in the position of the maximum and the extinction coefficient of the visible absorption band. The compounds do not appear to be a rapidly equilibrating mixture of oligomers. Rather, the preparations may vary in the average lengths and length distribution of the oligomeric products.

The crystal structure of PPB and the comparative studies of the solution properties of blue platinum compounds discussed above have established the features common to blue platinum complexes. What remains unclear is the basis for the blue chromophore. Comparative ESR and spectrophotometric titrations demonstrate that the chromophore arises from a transition to or from the orbital housing the unpaired spin. The ESR parameters and single-crystal measurements show this unpaired spin to reside in a d_{z^2}-derived molecular orbital directed along the mean Pt_4 chain axis.[11b] The blue chromophore shows large variations in intensity and wavelength as a function of the amidate ligands coordinated, the conditions of synthesis, the size of the oligomer, and, additionally, the presence of potentially coordinating anions. A definitive assignment for this transition must take into account this unusual sensitivity to experimental conditions. Perhaps it is distortions from the linearity in the platinum chain that affect this transition, either through axial ligand coordination or the canting of platinum coordination planes having both bridged and nonbridging ligands. It is interesting to note that blue platinum complexes having a stoichiometry of two amides per platinum, for example, PAB and the oxamate blues,[7] exhibit large extinction coefficients while the *cis*-diammineplatinum amide blues show extinction coefficients on the order of 100 M_{Pt}^{-1} cm^{-1}. Single-crystal polarized spectroscopic studies are needed to clarify the molecular orbital scheme.

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Molecular, Electronic, and Crystal Structure of Naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]thiadiazine

Alfred Gieren,* Viktor Lamm, Robert C. Haddon,† and Martin L. Kaplan†

Contribution from the Max-Planck-Institut für Biochemie, Abteilung für Strukturforschung I, Am Klopferspitz, D-8033 Martinsried, West Germany, and Bell Laboratories, Murray Hill, New Jersey 07974. *Received March 30, 1979*

Abstract: Naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]thiadiazine (**1**) crystallizes in the form of long, thin, lustrous, metallic green needles. The unit cell is monoclinic ($Z = 2$) with the $P2_1/a$ space group, and the lattice parameters are $a = 14.935$ (8) Å, $b = 8.304$ (6) Å, $c = 3.794$ (4) Å, $\beta = 91.53$ (7)°. In fact the molecule adopts the higher D_{2h} point group symmetry. The molecular geometry shows that **1** is heavily cross conjugated with a relatively small contribution from the structure corresponding to a naphthalene nucleus with peri-fused sulfurdiimide bridges. Strong bond-length alternation is found in **1**, particularly around the periphery of the molecule. The molecules form stacks in the *c* direction with a pseudohexagonal packing. Along the stacks the molecular planes are within a distance of 3.40 Å and the atoms are positioned similarly to those in the rhombohedral modification of graphite. The stacks are connected by two pairs of short intermolecular S···N contacts (3.104 Å), which leads to a ribbon-like array of nearly coplanar molecules. The intermolecular interaction takes the form of a parallelogram with sides composed of the intramolecular S–N bond (1.649 Å) and the S···N intermolecular contact (3.104 Å). Reference to the literature shows that short intermolecular chalcogen–nitrogen contacts occur in many compounds containing the -NSN- linkage. Furthermore, there is found to be a strong inverse correlation between the lengths of the intramolecular S–N bonds and the intermolecular S···N contacts, and possible reasons for this behavior are discussed.

Introduction

Recently the synthesis and the chemical and physical properties of naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]thiadiazine (**1**) have been reported.[1] The compound has a chemical stability indicative of aromatic character. On the other hand, physicochemical results (electrochemical behavior, electronic spectrum, and ^{1}H NMR chemical shift) suggest antiaromatic character. On this basis it was concluded that **1** is a compound of ambiguous aromatic character. In order to further elucidate the molecular and electronic structure of **1** we have carried out an X-ray structure analysis in the course of a systematic study[2a-k] on sulfur–nitrogen multiple bond systems.

Experimental Section

The title compound crystallizes from 1,2-dichloroethane in the form of long, thin, lustrous, metallic green needles. On the basis of Weissenberg and precession photographs the monoclinic space group $P2_1/a$ was determined from the $2/m$ symmetry of the reflections and the systematic absences ($h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$). The photographs show that the compound tends to form twinned crystals with (100) as the twinning plane. In order to determine the lattice parameters and to measure the intensities we used a punch-tape controlled automatic single crystal diffractometer (Siemens AED).

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† Bell Laboratories.

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