Fe$\cdots$Cl distance is ca. 4.1 Å. Cis O$\cdots$O interactions are found at 2.8–2.9 Å.

In the AIC solutions, the average Fe^{3+} is pseudotetrahedrally coordinated. In the 4.9 *m* solution, the average Fe^{3+} has ca. 3.5 chloride and ca. 0.5 water nearest neighbors, while in the 5.7 *m* solution the average Fe^{3+} has 4.0 chloride nearest neighbors. The inner-sphere Fe–Cl distance is ca. 2.28 Å. The nonbonded Cl$\cdots$Cl interaction, supporting the tetrahedral coordination of Fe^{3+} in the AIC solutions, is clearly discernible at $(8/3)^{1/2}(2.28$ Å). Solute association via chloro bridging occurs in each AIC solution, and the extent of solute association is dependent upon the AIC concentration. It is beyond the scope of these solution diffraction experiments to determine if solute association leads to the dimer (Fe_2Cl_6) or to an extended solute species $(FeCl_3)_n$, although the former is more consistent with the ARDF's than is the latter.

The nearest-neighbor environments of Fe^{3+} found in crystalline $FeCl_3\cdot 6H_2O$ and in crystalline $FeCl_3$ are retained for at least several weeks after each salt has been dissolved to prepare these concentrated aqueous solutions. The solute species initially formed in one (or both) set(s) of solutions may best be described as a kinetic product, with equilibration to the thermodynamic product being quite slow.

Registry No. $FeCl_3\cdot 6H_2O$, 10025-77-1; $[Fe(OH_2)_6]Cl_3$, 57533-67-2; $FeCl_3$, 7705-08-0.

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Trimethylacetamide Platinum Blue

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The nature of the dichloroplatinum trimethylacetamide blue (form III) is discussed, in conjunction with results for the analogous "platinblau" and for *cis*-diammineplatinum α-pyridone blue. The methods used in this study include UV–vis spectral measurements complemented by extended Hückel molecular orbital (EHMO) calculations and Ce^{IV} redox titrations. The results suggest form III consists of a nonequilibrium mixture of oligomers of variable chain length in which there is strong Pt–Pt interaction and in which platinum is in an average formal oxidation state greater than 2. The spectral data underscore the similarity in the electronic properties of form III, platinblau, and α-PB. The EHMO calculations confirm that platinblau and form III are best not formulated as monomeric Pt^{IV} complexes.

Introduction

The so-called "platinum blues"[1] are exceptional for their intense color which contrasts with the paleness of most platinum complexes. They have also aroused particular interest because of the antitumor properties of some of the complexes without the severe nephrotoxicity of *cis*-$PtCl_2(NH_3)_2$.[1] In this report we present findings concerning the nature of platinum blues and the origin of their extraordinary color. The study was centered on the trimethylacetamide platinum blue (form III) reported by Brown et al.[2,3] Results are also presented for "platinblau"[4–6] and the recently reported *cis*-diammineplatinum α-pyridone blue[7] (α-PB). The latter is exceptional because it is, to date, the only platinum blue fully characterized structurally.

The approaches used in this investigation include the use of potentiometric titrations with Ce^{IV} to gain information on the platinum oxidation state in blues, a study of the electronic spectra of the blues as a function of medium and temperature, and interpretation of the spectral data with extended Hückel calculations.

Experimental Section

Absorption studies in the UV–vis range were made on a Cary 17 Dx spectrophotometer. Low sample temperatures were obtained with an Lt-3-110 Liquid Helium Transfer Heli-Tran.

NMR spectra were recorded on a Hitachi Perkin-Elmer R20-B spectrometer and IR spectra (4000–250 cm^{-1}) on a Perkin-Elmer PE-457 IR spectrometer. Magnetic susceptibility measurements were carried out with a Cahn Instruments Faraday magnetic susceptibility system.

Elemental analyses were performed by Galbraith Laboratories, Inc., and by Integral Microanalytical Laboratories, Inc. Molecular weights were determined by vapor-pressure depression (Galbraith Laboratories).

Syntheses. The starting materials, *cis*-$PtCl_2(NH_3)_2$[8] and *cis*-$PtCl_2(CH_3CN)_2$,[9] were prepared by the literature methods, with minor modifications.

cis-Diammineplatinum α-pyridone blue was prepared by the method of Barton et al.[7] (Anal. Calcd for $[Pt_2(NH_3)_4(C_5H_4ON)_2]_2(NO_3)_5\cdot H_2O$: C, 14.82; H, 2.61; N, 14.69. Found: C, 14.90; H, 2.60; N, 14.17.)

Platinblau was synthesized from *cis*-$PtCl_2(CH_3CN)_2$ as reported by Hofmann and Bugge.[4] However, the dark blue or purple powders obtained by this procedure have elemental compositions which do not

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[1] J. P. Davidson, P. J. Faber, R. G. Fischer, Jr., S. Mansy, H. J. Peresie, B. Rosenberg, and L. Van Camp, *Cancer Chemother. Rep., Part 1*, **59**, 287 (1975).

[2] D. B. Brown, M. B. Robin, and R. D. Burbank, *J. Am. Chem. Soc.*, **90**, 5621 (1968).

[3] D. B. Brown, R. D. Burbank, and M. B. Robin, *J. Am. Chem. Soc.*, **91**, 2895 (1969).

[4] K. A. Hofmann and G. Bugge, *Ber. Dtsch. Chem. Ges.*, **41**, 312 (1908).

[5] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 2835 (1964).

[6] A. K. Johnson and J. D. Miller, *Inorg. Chim. Acta*, **22**, 219 (1977).

[7] J. K. Barton, H. N. Rabinowitz, D. J. Szalda, and S. J. Lippard, *J. Am. Chem. Soc.*, **99**, 2827 (1977).

[8] S. C. Dhara, *Indian J. Chem.*, **8**, 193 (1970).

[9] K. A. Hofmann and G. Bugge, *Ber. Dtsch. Chem. Ges.*, **40**, 1772 (1907).

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correspond to the proposed[2] formulation, $Pt(CH_3CONH)_2{\cdot}H_2O$ [for example: Anal. Calcd: Pt, 59.21; C, 14.59; H, 3.07; N, 8.54. Found: Pt, 59.95; C, 11.85; H, 1.90; N, 8.55 (or $PtC_{3.2}H_{6.18}N_{2.07}$)]. These and other notable differences are elaborated in the Results and Discussion section.

The dichloroplatinum trimethylacetamide blue (form III) was prepared by the method of Brown et al.[3] This procedure also yields two other dichloroplatinum trimethylacetamide complexes (forms I and II)[3] which are yellow. The synthesis was carried out as follows.

$Pt(CH_3CN)_2Cl_2$ and trimethylacetamide (TMA) (Aldrich Chemical Co.) were ground together in a 1:4 molar ratio. This mixture was then placed in an open beaker and brought slowly to 130 °C in an oil bath. At this temperature TMA readily sublimes, and the mixture must be periodically stirred to keep the reactants mixed. The melt is heated until it turns green-brown. The products are extracted with ether, and the ether solution is then evaporated to dryness. Excess TMA was sublimed from the products by heating them to 60 °C at a pressure of 30 μm for 24 h. The products were then dissolved in $CHCl_3$ and eluted through a 70–230-mesh silica gel column 1 cm in diameter and about 25 cm long. Elution rates were 5–10 mL of solvent/min.

Elution with $CHCl_3$ results in the gross separation of yellow crystalline components, forms I and II, and a mixture of blue compounds which are generally held by the column. Elution with ether removes one mixture of blue compounds, while elution with MeOH removes the others. All the blue products are amorphous and range in color from purple to blue to blue-green.

Forms I and II can effectively be separated by again eluting the yellow fraction, obtained above, through a silica gel column with $CHCl_3$. The first product off the column is form I. However, the separation between forms I and II is not always visible to the eye, and several fractions should be taken.

Form III, as characterized by NMR, is found among the blue products from the above separation. Its separation and identification are not always reliable due to the variety of possible blue products which are apparently formed. Elemental analyses of form III deviate significantly from that expected for the formulation $PtCl_2(TMAH)_2$ (Anal. Calcd: Cl, 15.21; N, 6.01; C, 25.76; H, 4.32. Found: Cl, 14.62; N, 6.83; C, 24.87; H, 4.30).

The yield of all three products is low, 5 g of $Pt(CH_3CN)_2Cl_2$ leading to about 250 mg of form I, 250 mg of form II, and 10–50 mg of form III. In particular, the yield and reliability of obtaining form III is so low as to render the above impractical as a synthetic method.

The yield of form II seems to increase with the amount of time the original reaction mixture is heated. Form II is the most unstable, and unless it is very pure, it tends to become green in solution or in the solid state. This problem also occurs with form I, but to a lesser extent.

It is also interesting to note that the reaction mixture, before elution on the silica gel column, visibly contains no blue products. In fact, when it is dissolved in ether or $CHCl_3$, it turns reddish brown. Once the products come into contact with the silica gel column, the mixture becomes deep blue. This indicates that the presence of silica gel is required for the formation of the blue complex.

Blue products have also been obtained, although not as a synthetic route, via a mixture of $Pt(CH_3CN)_2Cl_2$ and TMA in MeOH. If the mixture is allowed to stand for several weeks at room temperature, blue products appear, but only in the presence of silica gel. The TMA platinum blue II complex (TPB II), a variant of form III, is prepared in a water solution rather than in the melt.[1] A 1:2 molar ratio of $Pt(CH_3CN)_2Cl_2$ and TMA was stirred at 60 °C for 4 h in 200 mL of H_2O, during which a blue precipitate formed and the solution became yellow. The blue complex was filtered off, and the yellow solution was left standing at room temperature. Next, the product was dissolved in a minimum amount of acetone and reprecipitated by addition of H_2O. The product appeared to be contaminated with a large amount of grey solid which was never fully identified but was assumed to be a hydrolyzed form of the acetonitrile complex.

A less contaminated product could be obtained from the filtrate, which, if allowed to stand for a period of 1–2 weeks, yielded a significant amount of blue product. This was dissolved repeatedly in a minimum amount of $CHCl_3$, and the solution was filtered to remove impurities.

Addition of $AgNO_3$ to the reaction mixture showed a significant amount of AgCl precipitate. The filtrate also had become quite acidic. This tends to indicate that the product obtained contains hydroxy groups formed by the replacement of one or both of the chlorides. Elemental analysis did not agree with any simple empirical formula, indicating the formation of a polymer or a mixture of different products (Anal. Calcd for form III: C, 26; N, 6.0; H, 4.3. Found: C, 22.05; N, 5.88; H, 3.74).

Titrations. The titrations were monitored potentiometrically by using platinum vs. calomel electrodes. They were performed with no added heat and no protection from the atmosphere. The titrant was Ce^{IV} (4.94×10^{-3} N in 0.72 N H_2SO_4). The titrand was acidified with HCl so that $[HCl] \approx 4.5$ N. The presence of this acid, but not of chloride ion alone nor H_2SO_4, leads to rapidly stable voltage readings after each addition of titrant in the titration of K_2PtCl_4. Typically, the titrand was prepared by adding 35 mL of H_2O followed by 25 mL of concentrated HCl to the sample (in solid form or as a few milliliters of solution). Reaction of the titrated platinum complex with chloride ion should not affect our results concerning the average oxidation state of platinum in that complex since the total amount of reducing platinum species is expected to remain unchanged. In particular, since chloride ion is both a poor reducing agent and a poor oxidizing agent, it is most likely to affect the oxidation state of a blue, if at all, via disproportionation to Pt^{II} and Pt^{IV}, thus leaving the average oxidation state of the platinum in the titrand unchanged.

The titrations of K_2PtCl_4, *cis*-$PtCl_2(NH_3)_2$, and our sample of platinblau in each case yield titration curves displaying a sharp end point. Control experiments indicate that the oxidation of free acetamide is not involved for platinblau.

In the titration of K_2PtCl_4, very stable voltages are obtained usually within 1 min of each addition of Ce^{IV} solution. This is not the case in the titration of α-pyridone blue. Upon addition of Ce^{IV} solution, the voltage rises sharply and then decays for many minutes. The same effect is observed if K_2PtCl_4 is titrated in the presence of α-pyridone. However, a reasonable value for the end-point volume is obtained if a reading is taken after an arbitrary time (e.g., 1 min) has elapsed after addition of titrant. For example, the end-point volume is 3% higher than that expected for K_2PtCl_4 titrated in the presence of α-pyridone, if $[\alpha\text{-P}] = 3.3 \times 10^{-4}$ M in the titrand and $[\alpha\text{-P}]_{init}/[K_2PtCl_4]_{init} = 1.4$. In such cases, it is thus important to use a predetermined and consistent addition schedule in each titration.

Titration of α-pyridone alone yields no end point. Instead, upon each addition of titrant, the voltage rises to above 800 mV and then slowly decays.

Results and Discussion

A. Form III Results. A model describing the chloroplatinum trimethylacetamide blue or form III must explain the following results for this complex. (1) The molecular weight as measured by vapor-pressure depression in chloroform was found to be 1058 ± 15% for a sample of form III and 502 ± 5% for a sample of TPB II (see Experimental Section), a variant of form III.[10] The former value suggests a polynuclear structure, while the latter low value is close to the molecular weight of the monomeric structure formulated by Brown and co-workers[3] [$PtCl_2(CH_3CONH_2)_2$, mol wt 466]. (2) The molecular weight and extinction coefficients (UV–vis absorption spectra) are concentration independent at concentrations above $\sim 10^{-4}$ M. However, at lower concentrations, some deviation from Beer's law is observed.[10,11] (3) The UV–vis spectrum varies from one batch of form III to another. (4) The complex is intensely colored in the solid state and in solution. The temperature dependence of the spectrum of form III in a film of poly(methyl methacrylate) (PMM) demonstrates that electric dipole allowed transitions dominate the visible and UV regions.

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(10) Molecular weights were determined in $CHCl_3$ at the following concentrations: 0.0075, 0.0130, and 0.0176 M for TPB II; 0.0012 M for form III. Concentrations are based on a molecular weight of 466.

(11) (a) A sample of form III obeyed Beer's law in the range of concentrations used, 8.3×10^{-4}–8.3×10^{-5} M (based on a molecular weight of 466). Another sample of form III obeyed Beer's law upon changing the concentration from 6.3×10^{-4} to 1.9×10^{-4} M but showed a significant deviation in going from 1.9×10^{-4} to 2.0×10^{-5} M. (b) A sample of form III prepared by other workers showed a deviation from Beer's law upon varying its concentration in chloroform from 5.4×10^{-4} to 2.5×10^{-5} M (private communication by Professor David B. Brown, University of Vermont).

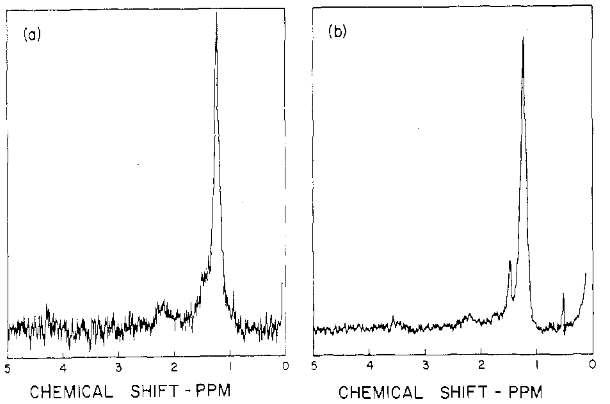

Figure 1. Proton NMR spectrum in CDCl$_3$ of (a) form III and (b) TPB II, a variant of form III.

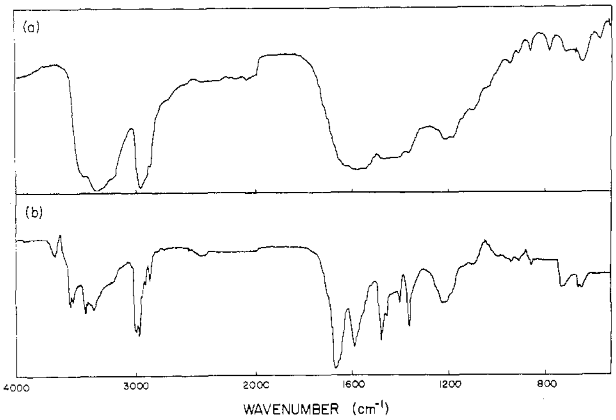

Figure 2. IR spectrum of form III in (a) KBr and (b) CHCl$_3$.

The spectral data is presented in section C. (5) The proton NMR signal for the TMA methyl groups is a relatively broad band[3] (δ 1.23 in CDCl$_3$, Figure 1). On the other hand, the corresponding band for form I is sharp, as it is for the uncomplexed TMA (δ 1.22 in CDCl$_6$ for both compounds).[3] (6) The IR spectrum in KBr (Figure 2a) shows only a broad envelope of bands which are very difficult to assign. The region below 400 cm^{-1} displays a single peak (323 cm^{-1} for form III, 328 cm^{-1} for TPB II, Nujol mull) which can be assigned to Pt–Cl stretching modes. However, its broadness (width at half-maximum is 46 cm^{-1} for form III and 54 cm^{-1} for TPB II) precludes the reliable differentiation of *cis*- and *trans*-PtCl$_2$ configurations on the basis of the number of Pt–Cl stretching bands (two for cis, one for trans) since typically for cis complexes ν_{sym}(Pt–Cl) – ν_{asym}(Pt–Cl) = 20 cm^{-1}.[12] These features seem indicative of a mixture of ligand environments due to polymerization or a mixture of products. The IR spectrum in CHCl$_3$ (Figure 2b) reveals more detail. The four bands in the region from 3600 to 3400 cm^{-1} are assigned to NH$_2$ stretching modes of the TMA ligand, while the band at 1670 cm^{-1} is thought to be the amide carbonyl stretch. (7) The X-ray powder diffraction pattern of form III is characteristic of an amorphous substance. (8) ESR measurements in the solid state at temperatures down to 4 K and magnetic susceptibility measurements at 25 °C showed no evidence of unpaired electrons (this is also the case for forms I and II).

Similar results are obtained for platinblau, except for (8),[12] above. This will be discussed elsewhere.

A model consistent with this data is obtained if form III is formulated as a mixture of oligomers involving platinum chains of varying lengths, with acetamido, chloride, and possibly hydroxy ligands, in the case of the variant form, coordinated to the metal. The platinum–platinum interaction in the chains can give rise to the intense color (vide infra). The low molecular weight (502) measured for the form III variant can be explained by an equilibrium of the type shown in eq 1, where M is a mononuclear moiety, L is a species which does

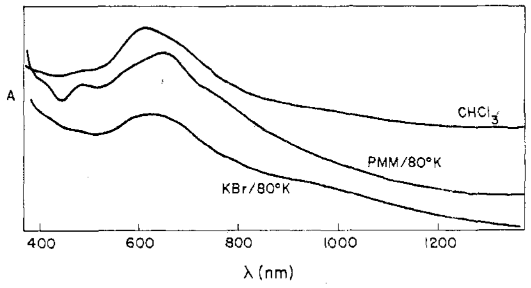

Figure 3. Electronic spectrum of form III in KBr, poly(methyl methacrylate), and CHCl$_3$.

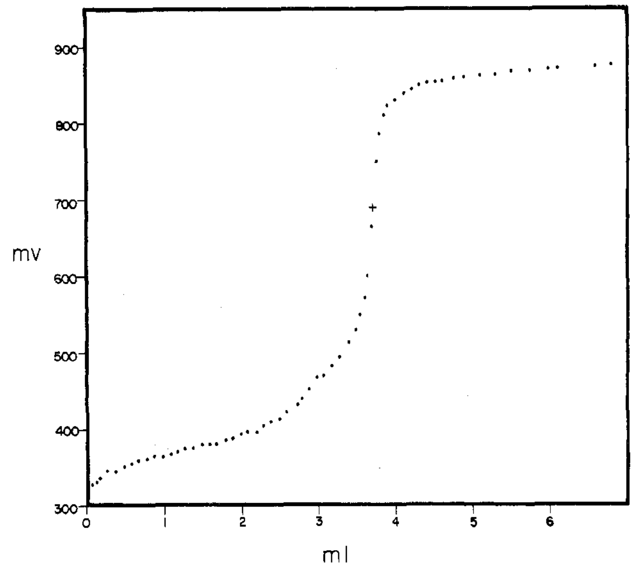

Figure 4. Titration curve of platinblau with Ce^{IV} in 4.5 N HCl. The equivalence point corresponds to 0.991 equiv of oxidant/mol of platinum.

$$M_n \overset{K_n}{\rightleftharpoons} M_n + (n-1)L \qquad (1)$$

not contain platinum, and n = 2, 3, etc. A similar process may be surmised for form III since its average molecular weight corresponds only to that of a binuclear species. The retention of Pt–Pt interaction in the dissociation process leads to preservation of the intense blue color of the solid in solution, although the solid state and solution spectra are similar but not identical (Figure 3). The observed deviation from Beer's law at low concentrations ($<10^{-4}$ M) may arise from partial dissociation of the chains themselves.

The broadening of the proton NMR band corresponding to the TMA methyl groups is also explained by this equilibrium and/or the presence of a mixture of polymeric products.

The magnetic properties of form III suggest that it contains platinum(II) or platinum(IV). ESCA data for form III are consistent with the presence of Pt^{II}.[14]

B. Titrations with Ce^{IV}. The platinum oxidation state is expected to be a key factor in understanding the properties of the blues. The redox titration technique is a method of

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(12) See, for example, U. Belluco, "Organometallic and Coordination Chemistry of Platinum", Academic Press, New York, 1974, p 54.

(13) Work in progress.

(14) D. F. Cahen, Ph.D. Thesis, Northwestern University, 1973.

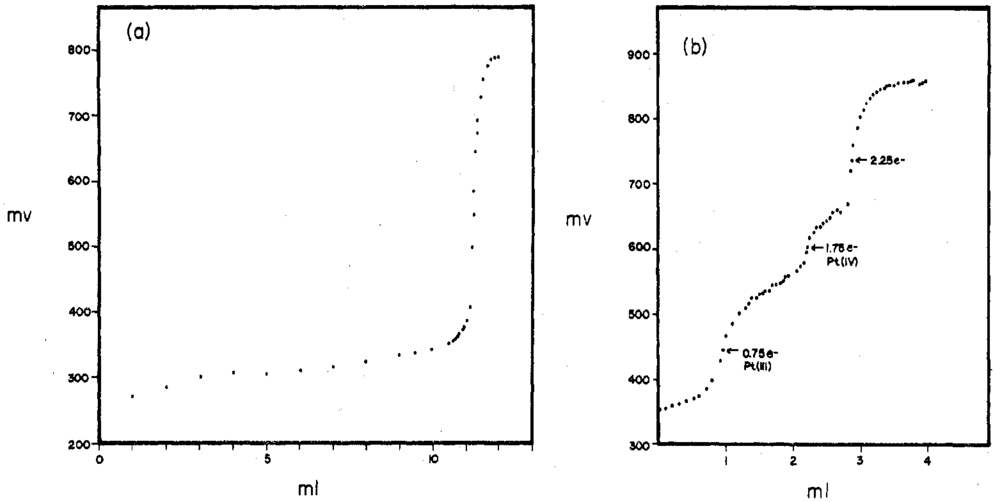

Figure 5. Titration curve of (a) *cis*-$PtCl_2(NH_3)_2$ and (b) *cis*-diammineplatinum α-pyridone blue with Ce^{IV} in 4.5 N HCl.

Table I. Titration of Some Platinum Complexes in 4.5 N HCl with Ce^{IV}

compd	oxidn state[c]	compd	oxidn state[c]
K_2PtCl_4	2.01	platinblau (ours)	3.01[b,d]
cis-$PtCl_2(NH_3)_2$	2.03[a]		

[a] See Figure 7. [b] See Figure 6. [c] Formal average oxidation state of platinum atom. [d] At the end point the solution is green. We believe the platinum was oxidized completely, i.e., oxidized to Pt^{IV}, in this titration because (i) the titration curve displays only one inflection upon addition of 2.7 equiv of oxidant/mol of platinum, (ii) the potential after the equivalence point has values close to those obtained in a titration of K_2PtCl_4 by the same method, indicating the Ce^{IV} "sees" no additional reducing species, and (iii) Ce^{IV} is a powerful oxidizing agent capable of oxidizing even chloride ion, though at a rate too slow to affect the present measurements (see, for example, H. A. Laitinen, "Chemical Analysis", McGraw-Hill, New York, 1960, Chapter 20). The titration data could also allow one to infer the following. (a) Pt in platinblau is Pt^{II} with half of it being unreactive toward Ce^{IV}. (b) The end product of the oxidation is a Pt^{III} derivative which is unreactive toward further oxidation by Ce^{IV}. These seem very unlikely possibilities.

Table II. Illustrative List of the UV-Vis Absorption Bands[a] for Samples of Form III and **TPB II** in $CHCl_3$

form III			TPB II		
λ, Å	ν, cm^{-1}	ε,[b] cm^{-1} M^{-1}	λ, Å	ν, cm^{-1}	ε,[b] cm^{-1} M^{-1}
8900	11 240	4300	6170	16 200	5500
6715	14 890	5900	4630	21 600	1800
5690[c]	17 500	3500	3750	26 700	1100
4420[c]	22 600	1700	3250	30 800	1500
2840[c]	35 200	2300			

[a] The electronic spectra of these substances vary from one synthetic batch to another. [b] Extinction coefficients are based on mol wt 466. [c] Shoulder.

Table III. Electronic Spectrum of Platinblau in Water at pH 7.4 (See Figure 6b)

λ, Å	ε, cm^{-1} L/mol of Pt	comments
8610	3600	
6740	3560	
5100		barely visible sh
4200		sh

Table IV. Visible-Range Electronic Spectrum of *cis*-Diammineplatinum α-Pyridone Blue (α-PB)[a]

λ, Å	ν, cm^{-1}	ε,[b] cm^{-1} L/mol of Pt
6820	14 660	1075
4770	20 960	416
4050[c]	24 690	220

[a] In 0.1 N HNO_3 (0.825 mg of α-PB/mL of solution; see Figure 6c). The complex is unstable in solution, decomposing over a period of hours. [b] Beer's law is not obeyed, ε increasing with concentration. [c] Shoulder.

choice because of its potential simplicity and precision. However, the water insolubility of form III makes its titration with a selective oxidant, such as Ce^{IV}, difficult. In light of this, we titrated a related compound, the acetamide analogue or "platinblau". The potentiometric titration of this compound with Ce^{IV} yields a titration curve with a sharp end point (Figure 4), from which an average oxidation state of 3.0 is calculated for the platinum atom. This value is to be contrasted with two others previously suggested for the oxidation state of the metal in platinblau. These are (1) an oxidation state close to +2, as indicated by X-ray photoelectron experiments which definitely ruled out platinum(IV),[15] and (2) an oxidation state of +4, as suggested by a kinetic study on the formation of platinblau from aqueous tetrachloroplatinate(II) in acetonitrile.[6] It is to be noted, however, that the platinblau synthesized for our study differs from the original platinblau of Hofmann and Bugge.[4] The very dark blue material has an elemental composition inconsistent with formulation as $Pt(CH_3CONH)_2{\cdot}H_2O$, and its average molecular weight in water is 372 rather than 329 as previously reported.[4] Even more surprising is its high magnetic susceptibility (530 × 10^{-6} cgsu/mol of Pt at 25 °C), since platinblau studied by Gillard and Wilkinson[5] was reported to be diamagnetic. The difficulty in reproducing the results of the Hofmann and Bugge synthesis have been pointed out by others.[3] However, the existence of diamagnetic and paramagnetic platinblau suggests that blues with different magnetic properties may still be closely related.

As a check on the validity of the Ce^{IV} titration method, well-characterized compounds were also titrated. The expected results are obtained for K_2PtCl_4 and *cis*-$PtCl_2(NH_3)_2$ (Table I, Figure 5a). On the other hand, the titration of α-PB yields a curve with three distinct inflections (Figure 5b). The first two correspond to $Pt^{2.25} \rightarrow Pt^{III}$ and $Pt^{III} \rightarrow Pt^{IV}$. The third and final inflection is presumably not connected with the

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(15) J. K. Barton, S. A. Best, S. J. Lippard, and R. A. Walton, *J. Am. Chem. Soc.*, **100**, 3785 (1978).

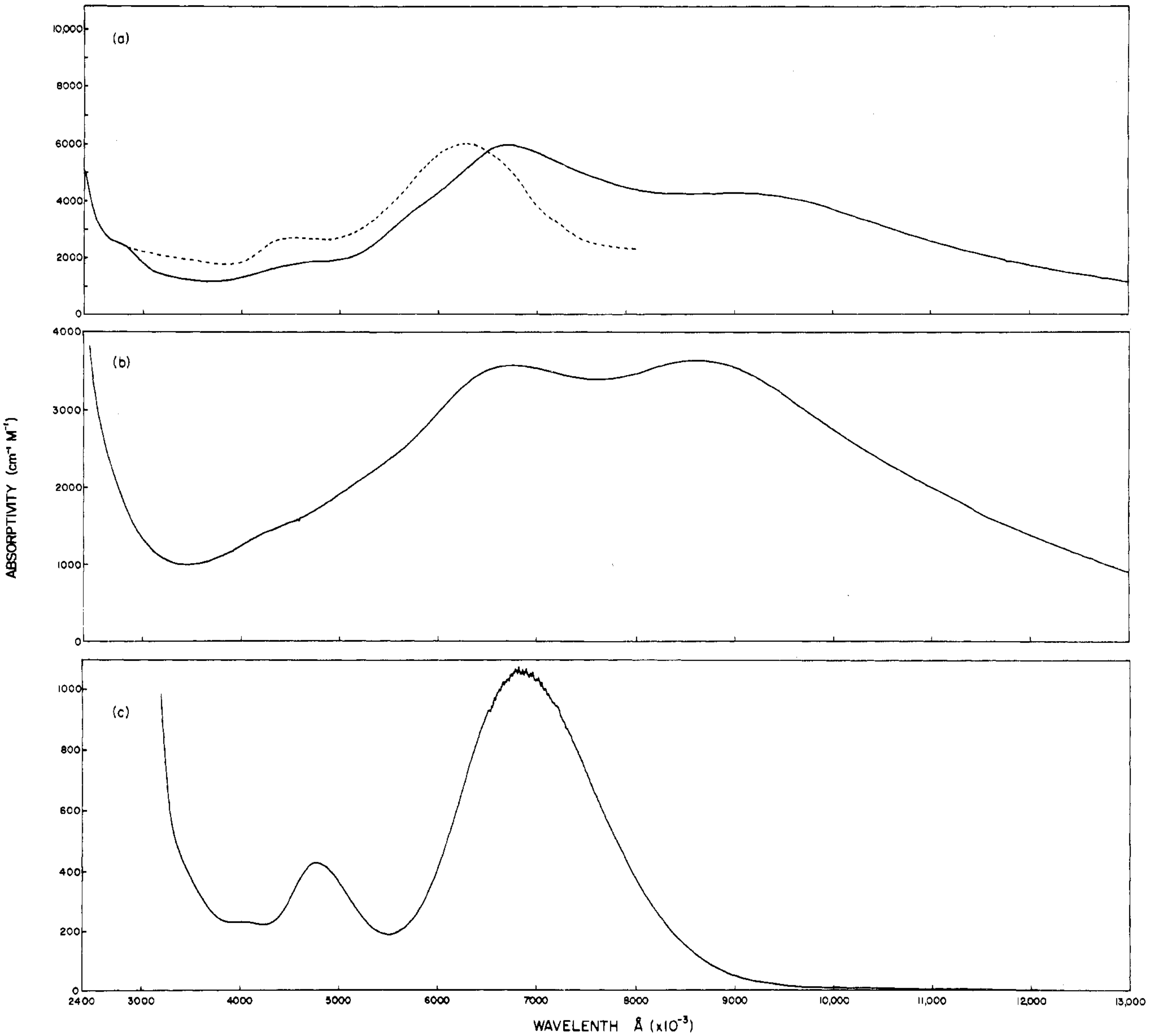

Figure 6. UV–vis range absorption spectra of (a) samples of form III and TPB II in $CHCl_3$, (b) platinblau in water (0.086 mg/mL, pH 7.4), and (c) *cis*-diammine α-pyridone blue in 0.1 N HNO_3 (0.28 mg of α-PB/mL of solution).

oxidation of platinum. It probably corresponds to partial oxidation of the ligands. The existence of a Pt^{III} intermediate in the oxidation of α-PB is significant in view of our findings for platinblau and the dearth of Pt^{III} complexes in general.[16]

C. Ultraviolet-Visible Absorption Measurements. The absorption spectra of form III, TPB II (Figure 6a, Table II), platinblau (Figure 6b, Table III), and α-PB (Figure 6c, Table IV) in the UV–vis region are similar. They exhibit absorption bands with extinction coefficients indicative of electric dipole allowed transitions. Absorption occurs throughout the visible and well into the IR region (7700 cm^{-1}, 13 000 Å) except for α-PB. In all cases the spectra show an increase in intensity of the band maxima as a result of the narrowing of the absorption bands upon cooling to 77 or 4 K. Therefore, electric dipole allowed transitions dominate the visible and UV portions of the spectrum.

It is of interest to note that the spectrum of the monomeric TMA complex, *trans*-$PtCl_2(TMA)_2$[3] (form I), is radically different from that of form III. It exhibits bands of low absorptivity which decrease in intensity with decreasing temperature, as expected for dipole-forbidden transitions. It is similar to the spectrum of *trans*-$PtCl_2(NH_3)_2$, in which there is also no significant Pt–Pt interaction.

The spectra of α-PB and platinblau in pellets show a remarkable dependence on the matrix salt. The bands are shifted roughly in a direction following the position of the anion in the spectrochemical series. Thus, the maximum of the dominating broad band in the visible region is at a wavelength which varies with the pellet salt as follows. (1) For α-PB: KBr (7600 Å) > KCl (6950 Å) > H_2O (6800 Å) ≈ KNO_3 (6760 Å). (2) For platinblau: KBr (6707 Å) > H_2O (6500 Å) ≈ KCl (6482 Å) > KNO_3 (6320 Å).

This dependence suggests the existence of labile anionic ligands coordinated to platinum and undergoing ready substitution even in the solid state or the partial breaking of Pt–Pt chains, leading to coordination of a matrix salt anion to platinum. This is consistent with what is known for α-PB for two reasons. First, this compound in the solid state contains a nitrate ion loosely coordinated to each terminal platinum atom of the tetranuclear chain. Second, addition of chloride ion to an aqueous solution of α-PB discharges the color im-

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[16] F. R. Hartley, "The Chemistry of Platinum and Palladium", Wiley, New York, 1973.

Electronic Transition Energies

Observed (α-PB in KBr)	Calculated	Assignment
13300 cm^{-1}	(a) 11600 cm^{-1}	$L \longrightarrow d_z2 - d_z2$
	(b) 12400 cm^{-1}	$L \longrightarrow d_z^2 - d_z2$
	(c) 13875 cm^{-1}	$d_z2 + d_z2 \longrightarrow d_z2 - d_z2$
16700 cm^{-1}	(d) 17900 cm^{-1}	$L \longrightarrow d_z2 - d_z2$

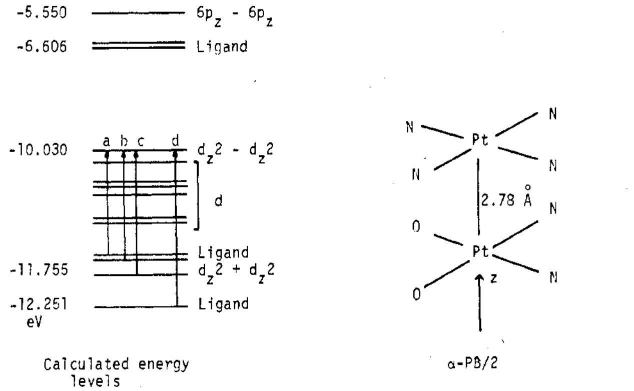

Figure 7. Calculated energy levels for α-PB/2 by the extended Hückel method and electronic-transition assignments.

mediately, as might be expected from scission of the platinum chain.

D. Extended Hückel Molecular Orbital Calculations. In order to gain a theoretical understanding of the peculiar spectral properties of the blues, we carried out extended Hückel molecular orbital (EHMO) calculations for α-pyridone blue. This compound was chosen because it is structurally characterized.[7] For practical reasons the calculations were performed on only half of the molecule, $Pt_2(NH_3)_4(C_5H_4ON)_2$ (α-PB/2), excluding also the nitrate groups. Furthermore, the formal platinum oxidation state was taken as 2 rather than the actual 2.25. The results of the calculations[17] are summarized in Figure 7.

The highest occupied molecular orbital is composed of d_{z^2} platinum atomic orbitals; this is expected since the d_{z^2} orbitals lie along the Pt–Pt axis. The platinum atom surrounded by four nitrogen atoms is less positively charged than the Pt atom coordinated to oxygen and nitrogen atoms, as is reasonable from electronegativity considerations.

The results for α-PB/2 can be tentatively extrapolated to yield a model for the entire α-PB molecule. Thus, it is expected that if the average oxidation number of platinum in α-PB/2 were increased to 2.25, 0.5 e would be removed from the $d_{z^2} - d_{z^2}$ orbital. Projecting this to the entire molecule leads to removal of 1 e from a $d_{z^2} - d_{z^2}$ type orbital to yield a doublet state. This is expected to increase the bonding between platinum atoms since the $d_{z^2} - d_{z^2}$ orbital is the antibonding counterpart of the $d_{z^2} + d_{z^2}$ orbital which represents Pt–Pt σ bonding interaction.

Emptying the low lying $d_{z^2} - d_{z^2}$ orbitals leads to a whole new series of electronic transitions which may explain the exceptional color of α-PB. Using the orbital energies calculated for α-PB/2, we have matched calculated and experimental transition energies (Figure 7). On the basis of this model, the bands of α-PB in the visible region involve ligand to metal transitions, although the band at 14 500 cm^{-1} could also arise from a $d_{z^2} + d_{z^2} \leftarrow d_{z^2} - d_{z^2}$ transition.

The model also predicts a series of low-energy (1500–7500-cm^{-1}) bands involving d–d transitions. These were not observed. Pellet (KBr, KCl, and KNO_3) spectra of α-PB show no distinct bands in the 5000–10 000-cm^{-1} range but just a steady increase in the absorbance assigned to scattering. The spectrum of α-PB in 0.1 N HNO_3 shows no absorption ($\epsilon < 5$ cm^{-1} L/mol of Pt) between 7700 (solvent cutoff) and 9300 cm^{-1}, and the rapidly increasing absorption above 9300 cm^{-1} is clearly due to the tail from the intense band with a maximum at 14 650 cm^{-1} (6820 Å). The other blues (form III and platinblau) do show significant absorption even at 5000 cm^{-1} (ϵ 65 cm^{-1} L/mol for form III in $CHCl_3$, on the basis of mol wt 466). However, no discrete bands are observed. Instead, there is an essentially monotonic increase of the absorbance on going to higher energies.

Finally, EHMO calculations were also carried out for "$Pt(CH_3CONH)_2X_2$". This is a formulation which has been postulated for platinblau[3] (X = OH) and is similar to one postulated for form III[3] (X = Cl). The calculated lowest transition energy (38 600 cm^{-1} for X = OH and 38 400 cm^{-1} for X = Cl, $d_{xz} \rightarrow$ ligand) is much higher than the intense "blue" transition energy (~15 000 cm^{-1}). Thus, these results suggest that the formulation of platinblau and form III as mononuclear Pt^{IV} complexes is incorrect.

Conclusions

The results presented in this report are consistent with a model postulating the acetamide and TMA blues as a nonequilibrium mixture of variable chain length oligomers with strong Pt–Pt interactions and with platinum in an average formal oxidation state above 2. Bridging amido groups would further stabilize the Pt–Pt interactions. Thus, these compounds are viewed as very similar to α-PB, except that the latter can be isolated as a pure crystalline compound containing only one type of polymer. Other studies support this type of model.[5,18,19] Of particular note is the recently reported Pt–Pt distance of ~2.9 Å found in platinum uridine blues as determined by the EXAFS method.[20]

EHMO calculations confirm that platinblau and form III should not be formulated as monomeric Pt^{IV} complexes.

Similar calculations on α-PB suggest the anomalous bands in the visible region for this compound arise from transitions from ligand or metal d-type orbitals to the antibonding d_{z^2} molecular orbital. The similarity between the spectra of the α-pyridone, acetamide, and TMA blues in the visible range suggest that the same type of transitions are operative for these compounds and probably for other blues. These systems can be compared to others known to involve chains with Pt–Pt proximity. The color of such compounds deepens with decreasing Pt–Pt distance[21] and increasing chain length.[22] Thus, "monomeric" platinum complexes are usually pale in color. It is also of interest that no blues are known for Pd and Ni. These elements have less propensity than Pt to form unoxidized chains, no derivatives are known in which they exhibit partially oxidized chains with metal–metal distances comparable to those in the metal.[23] This correlates with the markedly lower standard heats of sublimation of Ni (101.6 kcal) and Pd (93

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(17) The charge-iterated extended Hückel method [R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963)] was used for all calculations discussed. The platinum basis functions are taken from Cotton and Harris [*Inorg. Chem.*, **6**, 369 (1967)], while the C, N, and O Slater functions are from Burns [*J. Chem. Phys.*, **41**, 1521 (1964)].

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kcal) relative to that of Pt (121.6 kcal).[24] This is significant since the heat of sublimation is a measure of metal–metal bond strength in the pure metal.

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Registry No. K_2PtCl_4, 10025-99-7; *cis*-$PtCl_2(NH_3)_2$, 15663-27-1; $[Pt_2(NH_3)_4(C_5H_4ON)_2]_2(NO_3)_5$, 62782-86-9; *trans*-$PtCl_2(TMA)_2$ (form I), 24411-25-4; *trans*-$PtCl_2(TMA)_2$ (form II), 24380-93-6; dichloroplatinum trimethylacetamide blue (form III), 24411-26-5; platinblau, 30685-25-7; *cis*-$Pt(CH_3CN)_2Cl_2$, 21264-32-4.

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[24] "Handbook of Chemistry and Physics", 59th ed., CRC Press, West Palm Beach, FL, 1978–1979, pp D73–4.

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Oxy and Thio Phosphorus Acid Derivatives of Tin. 1. Triorganotin(IV) Dithiophosphate Esters

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Twelve triorganotin dithiophosphate esters $R_3SnS_2P(OR')_2$, where R = C_6H_5 when R′ = CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, *n*-C_4H_9, *i*-C_4H_9, or C_6H_5, where R = CH_3 when R′ = CH_3, C_2H_5, *n*-C_3H_7, or *i*-C_3H_7, and where R = C_6H_{11} when R′ = *i*-C_3H_7, can be synthesized in high yield by the condensation of the organotin hydroxide with the *O,O′*-diorganodithiophosphoric acid to release water which is distilled azeotropically, or taken up in an alcohol solvent corresponding to the phosphoric acid ester group, or by the reaction of the triorganotin chlorides with an alkali-metal salt of the dithiophosphoric acid. The products are colorless, crystalline solids except for the trimethyltin derivatives which are oils. The synthesis of the diisopropyl ester in the triphenyltin series is accompanied by protodemetalation to yield the bis compound $(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$. Infrared spectral bands were assigned to $\nu(CO)$ (1170–1095 cm^{-1}), $\nu_{asym}(PS_2)$ (675–635 cm^{-1}), and $\nu(POR)$ (1015–965 cm^{-1}), but the $\nu_{sym}(PS_2)$ absorption obscures the $\nu_{sym}(SnC_3)$ modes. NMR $|^2J(^{119}Sn\text{–}C\text{–}^1H)|$ coupling constants for the methyltin series are consistent with four-coordinated tin in solution and mass spectral data with monomers. Tin-119m Mössbauer data, on the other hand, specify a five-coordinated structure for the methyltin but a four-coordinated structure for the cyclohexyl- and phenyltins. The triphenyltin ethoxy and isopropoxy derivatives behave identically in a variable-temperature Mössbauer study, where the slope of the temperature dependence of the log of the resonance area is consistent with a monomeric structure packed in the solid into a rather tight lattice. With the use of low-energy, lattice-mode Raman data in the effective vibrating-mass treatment, the molecularity of the vibrating unit is found to be monomeric. The predicted monomeric, monodentate structure for these two esters is extremely rare among dithiophosphate–metal systems.

Organotin compounds are powerful biocides and have found wide application as agricultural fungicides and miticides, surface disinfectants, anthelminthics, and marine antifouling agents.[1,2] A particularly intriguing idea is to combine the triorganotin moieties which show the strongest biocidal activity with organophosphorus moieties which are also known for their potent biocidal effect. The combination of the two kinds of biological activity in a single molecule could produce a still more powerful and lasting effect and prevent the problems associated with the development of tolerance to each kind.

Several model organotin dithiophosphorus systems suggest themselves as subjects for study. We initiate this series of papers with a description of the synthesis of the triorganotin dithiophosphate esters. This class of compounds was first introduced in 1955 and has been the subject of several patents describing applications as bactericides, insecticides, fungicides, etc.,[3-15] but a satisfactory answer to the question of the structure–function relationships in the known systems[16-19] has not yet been given. The systems are also of interest structurally[20] since several modes of attachment of the dithiophosphate ester ligand are in principle possible, including those of a monodentate, bidentate, or bridging ligand in an oligomeric form as in a dimer and that of a bridging ligand in an associated polymer chain. The X-ray crystallographic results for certain key examples will be published as a part of this series.

We report here the synthesis of 12 compounds, nine not reported before, by two preparative methods.[21]

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