were obtained. Attempts to obtain better crystals by slower recrystallization were unsuccessful.

Reaction of 1a with 4-Methylpyridine. 4-Methylpyridine (153 mg, 1.65 mmol) was added to **1a** (138 mg, 0.24 mmol) suspended in THF (5 mL), and the yellow suspension was stirred overnight. Solvent was removed and the yellow powder was extracted with toluene, giving a yellow-orange solution and a white powder. The white powder was identified as unreacted **1a** by its IR spectrum. The yellow-orange solution was evaporated to an orange powder. This material had no hydride band in its IR spectrum. When the orange powder was dissolved in C_6D_6 a white precipitate formed (probably hydride), and the spectrum obtained had a complex cyclopentadienyl region and no pyridyl resonances.

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Registry No. 1a, 80642-73-5; **1a′**, 80642-74-6; **1b**, 80658-44-2; **2a**, 88181-77-5; **2a′**, 88181-78-6; **2b**, 88200-37-7; **3a**, 88181-79-7; **3a′**, 88181-80-0; **4a**, 88181-86-6; **4b**, 88181-87-7; **5a**, 88181-88-8; **5b**, 88181-89-9; **6a**, 88181-81-1; **6b**, 88181-90-2; **7b**, 88181-91-3; **8a**, 88181-82-2; **8b**, 88181-92-4; **9a**, 88181-83-3; **10a**, 88181-84-4; **10b**, 88200-38-8; **11b**, 88181-93-5; **12a**, 88181-85-5; $[(C_5H_5)_2YCl]_2$, 57398-67-1; $[(C_5H_5)_2YCH_3]_2$, 60997-40-2; $[(C_5H_4CH_3)_2YCl]_2$, 80642-81-5; $[(C_5H_4CH_3)_2YCH_3]_2$, 72556-67-3; 3-hexyne, 928-49-4; *cis*-3-hexene, 7642-09-3; *cis*-stilbene, 645-49-8.

Supplementary Material Available: Tables of bond distances, angles, final fractional coordinates, thermal parameters, and structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

Synthesis, Binding Sites, and Spectroscopic Characterizations of Succinamic Acid and Succinimide Platinum Blues

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Abstract: By using K_2PtCl_4 and succinamic acid or succinimide new mixed-valent platinum blues have been obtained. By using ^{13}C NMR spectroscopy the compound, prepared from succinimide, has been identified as a succinamic acid blue, hydrolysis of the imide occurring during the course of the reaction. These compounds have been characterized by UV-visible spectral measurements, Ce(IV) oxidative titrations, XPS, and ESR spectroscopies. From the whole set of data so obtained the succinamic acid blues may be considered as a limiting case between class II and class III mixed-valence complexes.

The so-called "platinum blues" have attracted considerable attention for several years. In fact they are exceptional for their intense blue color in contrast to the yellow or colorless nature of most platinum complexes. Although blue platinum compounds were reported since 1908[1] and have been subject to extensive studies,[2] their nature remained elusive until single crystals of *cis*-diammineplatinum α-pyridone blue were prepared.[3] Extensive studies on this compound were carried out to determine the solid-state structure,[4] magnetic[4] and X-ray photoelectron spectroscopic[5] behavior, and chemical and spectroscopic properties in aqueous solution.[6] From these studies it has been inferred that at least three properties are shared by most of the platinum blues in solution as well as in the solid state: mixed valency, oligomerization, and amidate bridging. More recently arguments favoring a strong electronic delocalization along the platinum chains have been deduced from optical studies, and it has been suggested that the platinum blues are best described as class II–class III borderline or as delocalized class III mixed-valent compounds (according to Robin and Day's classification[7]) in which there is extensive delocalization but, at least in the case of the phthalimide blues,[8] inequivalent metal sites.

Table I. Elemental Analyses Data of Platinum Succinamic Acid and Succinimide Blues

	% C	% H	% N	% Pt	% Cl	% K
found for B						
batch 1	11.0	2.8	3.3	45.0	12.6	ϵ
batch 2	10.8	2.6	3.5	44.5	12.5	0.1
calcd for $[PtC_4O_3NH_6Cl_{1.5}\cdot 3H_2O]_n$	11.47	2.87	3.35	46.64	12.71	
found for (C)	12.3	2.7	3.6	50.9	4.5	0.3
calcd for $[PtC_4O_5NH_6Cl_{0.5}\cdot(OH)\cdot 2H_2O]_n$	12.57	2.88	3.67	51.10	4.64	

However, much of the interest devoted to these products stems in the fact that pyrimidine and amide blues were found to have a high index of antitumor activity and a low associated nephrotoxicity.[9–11]

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Most of the blue species already obtained have been prepared by reacting an amide with the hydrolysis products of *cis*-Pt$(NH_3)_2Cl_2$, and few works have been devoted to blue compounds obtained from other platinum precursors.[12] However, previous studies have demonstrated that K_2PtCl_4 may be used to prepare blue species.[13] New examples of this possibility are given in the present report where blue species resulting from the reaction of potassium tetrachloroplatinate with succinamic acid and succinimide are described.

Experimental Section

Preparation and Characterization of the Blue Platinum Complexes. The starting material, *cis*-$(NH_3)_2PtCl_2$, K_2PtCl_4, succinamic acid, and succinimide were purchased from Aldrich Chemical Co. and used without further purification.

***cis*-Diamminesuccinamic Acid Blue (A).** A 0.1 M solution of *cis*-diammineplatinum(II) hydrolysis products was prepared by mixing 0.3 g of *cis*-$(NH_3)_2PtCl_2$ and 0.34 g of $AgNO_3$ in 10 mL of water. After a night in the dark under stirring at room temperature the solution was centrifuged to remove any AgCl precipitate. One equivalent of succinamic acid dissolved in the minimum amount of water was then added to the filtrate without adjusting the pH. The solution was then incubated in the dark at approximately 25 °C. After 1 day a white precipitate may be observed while the filtrate remains colorless. This white product slowly disappears and the solution turns to a blue color. The incubation was continued for a month and the solution was then filtered to remove any white precipitate. Precipitation by a 80/20 mixture of $EtOH/Et_2O$ gives a blue precipitate that was collected by filtration. The compound was dried in a desiccator over anhydrous $CaSO_4$. The yield was low and elemental analyses differ from batch to batch; however, from the elemental analytical data it may be inferred that the ratio of platinum to ligand is always close to one.

Platinum Succinamic Acid Blue (B). The reaction of aqueous equimolar K_2PtCl_4 and succinamic acid (0.1 mol) dissolved in 10 mL of water and allowed to react at pH 7.2 for 2 h yields a dark blue solution. The pH value was monitored by addition of KOH (1 N). The blue powdered compound was collected by precipitation with an ethanol/ether mixture (80/20), redissolved in water, and precipitated again with the same solvents, this several times. It may be noticed that this product is very soluble in water during the course of the synthesis; however, after it has been dried in vacuo, it becomes practically insoluble. Elemental analyses data are given in Table I.

Platinum "Succinimide Blue" (C). The blue complex was prepared by dissolving 2×10^{-3} mol of K_2PtCl_4 in 10 mL of H_2O and filtering to remove any Pt(0); to this a concentrated basic solution of succinimide (2×10^{-3} mol, pH 10 by KOH) was added. The resulting solution was kept at 25 °C for 2 days, the pH being adjusted to 7.2 initially. A blue color appears rapidly and a blue powder can be precipitated by a mixture of ethanol/ether (80/20). After several dissolutions and precipitations, the analytical data reported in Table I were obtained.

If the whole synthesis was conducted at pH 7 only a green-grey precipitate of largely variable composition resulted. This fact will be discussed below.

As yet all attempts to obtain crystals of B and C or of their copper(II) salts (vide infra) failed. It is of interest to note that before each precipitation step, an absorption spectrum was recorded for compounds B and C. The only noticeable modification related to these successive precipitations was the disappearance of the band attributed to K_2PtCl_4. Similarly, the 1400–1700-cm^{-1} area of the infrared spectra remained unmodified. Furthermore, the ^{13}C NMR spectra, directly recorded on the reaction mixture (vide infra), did not provide any feature attributable to a carbon-containing contaminant. These observations do not preclude the hypothesis of B and C being mixtures of oligomers of varying lengths but involving the same basic structure.

Measurements. The infrared spectra of the ligand and complexes were recorded on a Perkin-Elmer Model 577 spectrometer calibrated with polystyrene film, using KBr disks. Electronic spectra were recorded on a Cary 14 spectrophotometer in the 800–200-nm range.

Table II. ^{13}C NMR Data of Ligands and Related Platinum Blues (ppm/Me_4Si)

	$\delta_{C=O}$			
	acid	amide	imide	δ_{CH_2}
NH_2-CO-CH_2-CH_2-COOH	181.3	179.6		32.08, 31.61
compound B	182.3	163.3		34.07, 33.16
succinimide CH_2-CO-NH-CO-CH_2			179.0	30.1
succinimide after $^1/_2$ h at pH 10	183.7	181.5	179.6	33.63, 32.46, 30.20
compound C	182.5[a]	163.2[a]	179.5	33.5,[a] 32.4,[a] 30.0

[a] Major species (see text).

The ESR spectra were obtained on a Brucker ER.200K with a conventional X-band (9.6 GHz). The microwave frequency was calibrated with diphenylpicrylhydrazyl. All ESR spectra were recorded on frozen aqueous solutions directly on the mother solution; they were also recorded on the powdered sample in a large range of temperature.

The X-ray photoelectron spectroscopic measurements were obtained with an AEI ES 200B spectrometer with Mg Kα radiation (1253.6 eV) as the X-ray excitation source, the powdered samples being compressed into a copper grid. The measured binding energies were standardized with a Au 4f 7/2 binding energy of 83.5 eV.

XPS spectra were deconvoluted with a program requiring input for the number of peaks and the length, half-width, and position for each peak suspected of comprising the multiplets. On the basis of these parameters, a spectrum is calculated that can be compared to the experimental spectrum. In all the deconvoluted spectra we have a good fit between calculated and experimental spectra. All the spectra were deconvoluted at last twice (for two different runs of the same sample). Agreement between two deconvolutions was excellent.

The NMR spectra were recorded on a WH 250 Brucker spectrometer operating in the Fourier transform mode and equipped with a wide band probe (23–103 MHz).

Typical parameters for ^{13}C spectra were the following: pulse width 20 μs, impulse delay 1 s; 100 accumulations were usually necessary to achieve a satisfactory signal-to-noise ratio. The ^{13}C spectra were recorded directly on the reaction mixtures, a special preparation being conducted in D_2O for this purpose.

The ^{13}C chemical shift observed for the succinamic acid and succinimide ligands as well as for the B and C blue complexes are collected in Table II.

Oxidative Titration. The solution of platinum blue is decolorized by a number of oxidizing agents, this observation provides a method of estimating the formal oxidation number of platinum in these compounds. Oxidative titration was monitored by spectrophotometry and carried out with ceric sulfate solutions (5.023×10^{-3} N in 0.70 N H_2SO_4) standardized with use of the normal procedure. The average oxidation state of the platinum atom was calculated on the basis of the percentage of platinum in the sample as determined by elemental analysis.

Results and Discussion

Synthesis. Succinamic acid reacts with the *cis*-DDP hydrolysis products to afford a blue species but the reaction rate and the yield are low. On the contrary when $PtCl_4K_2$ is used as platinum precursor the reaction with succinamic acid or succinimide is fast and an almost quantitative yield of blue species is obtained. The elemental analyses data related to both complexes are reported in Table I. In spite of some slight variations from batch to batch, these data fit the simple formulations $Pt_2L_2Cl_3 \cdot 6H_2O$ for B and $Pt_2L_2Cl(OH)_2.4H_2O$ for C, L being the deprotonated ligand $C_4H_6NO_3$. Analytical data for A imply also a platinum-to-ligand ratio near 1, but no reliable satisfactory formulation may be proposed. The formulae as well as the true nature of the A species seem to depend on the reaction time. It is noteworthy that in the case of C we assume the platinum atoms to be coordinated to succinamic acid molecules and not to succinimide. This hypothesis is supported by the NMR data and will be discussed later. In the two complexes the carboxylic function is free, the precipitation of the blue complex by a mixture of $EtOH/Et_2O$ seeming to avoid the obtention of the potassium carboxylates. It is difficult to obtain these carboxylates in basic media, the solution turning rapidly a brownish color at high pH. However, it is possible to obtain precipitation of B and C as stable copper(II) salts by adding $CuCl_2$ solutions to the reaction mixtures. These products are presently under investigation. We wish to emphasize that contrary to

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previous reports,[6] the B and C compounds are prepared in the presence of chloride ions. Furthermore, both species may be kept for some months in the mother solution without any apparent damage.

The electronic spectra of B and C are practically independent of the anions present in solution. Furthermore, they show the same pattern, i.e., a broad band centered at 625 nm.

^{13}C NMR Spectroscopy. Well-resolved ^{13}C NMR spectra have been obtained for the B and C species. It may be emphasized that these spectra directly recorded on the reaction mixtures display one set of signals in the case of the B while the C spectra exhibit a more intricate pattern.

For the succinamic acid itself two distinct C=O resonances are observed at 181.3 and 179.6 ppm, respectively; according to the literature data[14] the high-field signal is attributed to the amidic carbon while the low-field signal may correspond to the carboxylic acid carbon. In going from the free ligand to the B complex the low-field signal is little affected while the amidic carbon suffers a very important downfield shift (16 ppm). This shift strongly suggests coordination through the oxygen of the amide function, this effect being consistent with a lowering of the C=O bond order.

To interpret the spectrum of C, one has to consider first the spectra of the free succinimide at neutral and basic pH. At neutral pH two signals attributable to the carbonyl and the methylenic carbons are observed. Increasing the pH causes the appearance of a second set of signals which display chemical shift values almost identical with those observed in the case of succinamic acid. It is very likely that hydrolysis of the imide occurs and leads to the formation of the corresponding acid amide. With respect to this result, the six signals observed in the spectrum of C are likely due to a major species which displays a great similarity to B and to a small quantity of unreacted imide. It is well known that metal ions increase the rate of the hydrolysis process, and for the C species we are in concurrence not with an "imide blue" but with an acid amide one.

The similarity between B and C inferred from the NMR data is consistent with the formulation deduced from the analytical results which imply that in both species each platinum center is bonded to one acid amid molecule and to a variable number of Cl^-, OH^-, and/or OH_2 entities. Regarding the coordination site of the ligand, the important shift suffered by the amidic carbonyl strongly suggests that in both complexes this group is directly concerned in the coordination process.

To our knowledge, only one "imide blue complex" has been already reported in literature, i.e., the "platinum phthalimide blue".[6] In this case the reaction occurs at pH 1.2 and at 50–60 °C. Due to the lack of ^{13}C NMR data concerning this complex, it is difficult to envision either the existence of a "real imide blue" or the occurrence of an hydrolysis process providing the formation of an acid amide blue. In our case, we have prepared a blue compound using phthalic acid amide as the ligand, the study of which is still in progress.

Oxidative Titration Data. The oxidation of succinamic acid blue with use of Ce(IV) as the titrant has been monitored spectrophotometrically on different preparative batches yielding identical results. The blue absorption band decreases in intensity without any shift in its maximum. The end point is obtained with the addition of 1.52 ± 0.10 equiv of cerium per platinum atom, showing that the metal oxidation state is nonintegral in this blue species, and equal to 2.5 ± 0.1. Indeed, assuming an oxidation state of 2.5, the removal of $\simeq$1.5 electron by oxidation produces a platinum(IV) end product. These data may be related to those observed for other platinum blues and often obtained by ceric oxidation monitored either by potentiometry[8] or by ESR.[6-8] In the case of α-pyridone blue, the averaged oxidation state is 2.25 while in the phthalimide blue it varies from 2.9 to 3.2 according to different preparative samples.

X-ray Photoelectron Spectroscopy (XPS). To achieve the characterization of the succinamic acid blues, we have investigated their platinum XPS spectra. A typical Pt_{4f} spectrum of B appears in Figure 1 while Table III summarizes binding energy data for our blue complexes compared to some other platinum mixed-valence species. It may be emphasized that binding energies and peak shapes do not show any time dependence and that identical spectra have been obtained from different preparative batches.

Table III. Core Electron Binding Energies of Some Platinum Blues and Mixed-Valence Pt_{II}–Pt_{IV} Complexes

	Pt_{IV}		Pt_{II}		
	$Pt_{4f\,5/2}$	$Pt_{4f\,7/2}$	$Pt_{4f\,5/2}$	$Pt_{4f\,7/2}$	ref
K_2PtCl_4			77.9	74.6	
succinamic acid blue	79.7	76.3	77.9	74.5	*a*
Pt oxamate blue	77.3	74.1	75.7	72.3	15
$Pt_2(NH_3)_4(OH)_2(NO_3)_2$	78.7	75.5	76.9	73.6	16
Wolfram's red salt	79.8	76.4	77.4	74.1	17

[a] This work.

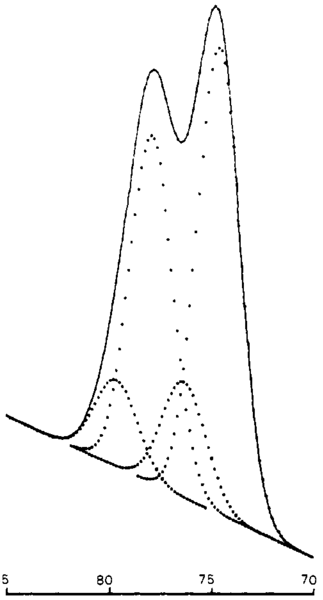

Figure 1. XPS spectrum of platinum succinamic acid blue (—) and deconvoluted peaks assuming the presence of two Pt signals (···).

The deconvoluted Pt_{4f} spectra comprise two doublets of unequal intensities (3/1). These two sets of signals are indicative of the simultaneous occurrence of two oxidation states which likely are Pt(II) and Pt(IV). The observed shift of ca. 2 eV in the $Pt_{4f\,7/2}$ energies is consistent with a two-unit change in the oxidation state of the platinum since values ranging from 1.8 to 2.3 are quoted in the literature.[15-17] Recalling that the intensities ratio (3/1) does not depend on time exposure and remains unaffected from batch to batch, it is unlikely that the occurrence of platinum(IV) would be due to an X-ray induced oxidation of platinum(II) centers as in the work of Stanko et al.[16] or to an impurity. Therefore the succinamic acid blues may be considered as actually involving three platinum(II) and one platinum(IV). This would lead to an average oxidation state of 2.5 which agrees with the values 2.5 ± 0.1 deduced from oxidative titrations.

The observation of two well-characterized oxidation state in the XPS spectra of succinamic acid blue is in marked contrast with the behavior of the α-pyridone blue.[5] In this case, only one oxidation state appears in the XPS spectra although two types of metal environments are revealed by the crystal structure. These data lead the authors to the conclusion that the unpaired electron responsible of the paramagnetism is largely delocalized over four

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Table IV. g Values of One-Dimensional Chain Compounds and Platinum Blues

	$g_{\parallel}$	$g_{\perp}$	ref
$[Pt(NH_3)_4][PtCl_4]$ (Magnus' green salt)	1.939	2.504	23
$K_2Pt(CN)_4Br_{1/3}\cdot 3H_2O$	1.946	2.336	24
Pt α-pyridone blue	1.976	2.380	4
uracil blue	1.99	2.40	18
succinamic acid blue	1.99	2.42	*a*

[a] This work.

platinum atoms—as suggested by extensive hyperfine coupling observed in the ESR spectra (solution).

ESR Spectroscopy. Judging from the ESR data, the B and C complexes are paramagnetic. Their powder or frozen solution spectra display two signals at ca. 2800 and 3400 G. The large shift ($g_{\perp} = 2.42$ and $g_{\parallel} = 1.99$) is likely attributable to a strong spin–orbit interaction which suggests that the paramagnetic centers are actually related to a metal ion.

Other platinum blues containing three-valent platinum have been studied in solution[6,18] and as powders[19] by means of EPR. To date only one single crystal EPR[4] study has been done, that of platinum α-pyridone blue, in which no hyperfine structure was observed. The differently measured g values are similar to those obtained for the one-dimensional chain compounds (Table IV), and spectra can be described by the following axial spin Hamiltonian,

$$\mathcal{H} = \beta\, g_{\parallel}S_zH_z + g_{\perp}(S_xH_x + S_yH_y) + A_{\parallel}S_zI_z + A_{\perp}\,(S_xI_x + S_yI_y)$$

where β is the Bohr magneton, S is the spin operator ($S = {}^1/_2$), H is the resonant magnetic field, A is the hyperfine tensor, and I is the total nuclear angular momentum operator. The observed g values for these different species are described by a $d_z{}^2$ hole state (z taken along the Pt chain axis) with an admixture of the lower-lying d_{xy}, d_{yz} state. Data from previous studies of platinum blues have been interpreted as suggesting that the electronic charge is either localized, yielding a Pt(III) ion,[20] or delocalized along a chain of two,[21] or more platinum centers.

By using the hyperfine coupling (100 to 400 G) expected for the interaction of the unpaired spin with the ^{195}Pt nuclei ($I = {}^1/_2$, natural abundance 33.8%) and the g values (2.42 and 1.99) we have found that, independently of the model employed for the simulation, the calculated spectra can always be fitted to the experimental ones by choosing a suitable value of the linewidth. However, if the simulation is restricted to reasonable values of the linewidth (6–8 G),[22] then an extensive but unresolved hyperfine coupling must be assumed. This suggests a delocalization of the spin over several platinum centers.

It is very often accepted that the occurrence of two distinguishable peaks in the XPS spectrum of a mixed-valence complex gives evidence of a trapped valence ground state while a single peak is predicted for a delocalized system. However, it has been pointed out[25] that this rationale may not be correct due to the fact that the core-photoionized state may no longer have a symmetrical charge distribution.[26,27] For instance, the XPS spectrum of the Creutzh-Taube complex exhibits two $Ru_{3d\,5/2}$ peaks, with energies corresponding approximately to those observed in single-valence Ru(II) and Ru(III) compounds of analogous structure, although there is good independant evidence of a delocalized ground state.[26] Thus, the observation of two distinguishable oxidation states in XPS spectra is not theoretically inconsistent with some degree of delocalization. In this instance, succinamic acid blues would no longer be basically distinguished from α-pyridone blue in spite of their different XPS spectra. In terms of the Robin and Day scheme, we may consider the α-pyridone blue belongs to class III while succinamic acid blues would be better described as class II–class III borderlines involving platinum(II) and platinum(IV).

Registry No. *cis*-$(NH_3)_2PtCl_2$, 15663-27-1; Pt, 7440-06-4; succinimide, 123-56-8.

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