spectra. We would also like to express our gratitude to Steven Carr and Dr. Catherine Costello for their aid in obtaining the mass spectra. Financial support from the Natural Sciences and Engineering Research Council of Canada (C.O.) and New England Nuclear (M.S.) is gratefully acknowledged.

Registry No. I, 75948-92-4; II, 75948-93-5; III, 75948-94-6; IV, 75948-95-7; V, 75948-96-8; VI (Ph_4As salt), 75949-45-0; VI (n-Bu_4N salt), 75949-46-1; VII (Ph_4As salt), 75949-48-3; VIII (Ph_4As salt), 75951-54-5; IX (Ph_4As salt), 75949-50-7; *N,N'*-ethylenebis(3-mercaptopropionamide), 818-41-7; *N,N'*-propylenebis(2-mercaptoacetamide), 75948-97-9; *N,N'*-propylenebis(3-mercaptopropionamide), 75948-98-0; *N,N'*-*o*-phenylenebis(2-chloroacetamide), 2810-42-6; *o*-phenylenediamine, 95-54-5; benzoyl chloride, 98-88-4; chloroacetyl chloride, 79-04-9; thiobenzoic acid, 98-91-9; NH_4TcO_4, 13598-66-8; *N,N'*-ethylenebis(2-mercaptoacetamide), 692-93-3.

Contribution from the Department of Chemistry,
University of Maine, Orono, Maine 04469

The Platinum Phthalimide Blues: Synthesis and Physical Characterization. Hush Model Interpretation of Optical Spectra

C. ALLEN CHANG, RONALD B. MARCOTTE, and HOWARD H. PATTERSON*[1]

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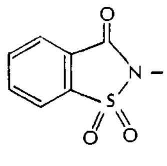
A new class of mixed-valent platinum blue compounds, prepared by using *cis*-dichlorodiammineplatinum(II) (*cis*-DDP) and potassium phthalimide, are characterized by UV–visible spectral measurements, Ce(IV) oxidative titrations, and other techniques. The formation of insoluble polymeric blue species is favored at higher temperatures and concentrations. By varying the mole ratio of starting materials, it is possible to obtain blue precipitates with different average platinum oxidation states. Semiquantitative calculations for the mixed-valence absorption profiles using Hush's formulas for class II weakly interacting MV systems indicate that this model fails to predict the half-bandwidth and the temperature dependence of at least the three platinum blues we have examined, i.e., platinum phthalimide blue, platinum α-pyridone blue, and Platinblau. All these blues with strongly interacting Pt–Pt centers are best described as class II–class III borderline or as delocalized class III mixed-valent compounds according to Robin and Day's classification.

Interest in blue platinum compounds started in 1908 when Hofmann and Bugge reported that "Platinblau" was formed in a reaction between dichlorobis(acetonitrile)platinum(II) and silver salts.[2] The compound was formulated as a monomeric platinum(II) complex, $[(CH_3CONH_2)_2Pt]\cdot H_2O$, and it was reexamined and proposed by Gillard and Wilkinson in 1964 to be polymeric with bridging amidate linkages.[3] In 1968, Brown et al. prepared a blue material by reacting trimethylacetamide with $[(CH_3CN)_2PtCl_2]$.[4,5] The blue material was formulated as the monomeric platinum(IV) complex, $[(t\text{-}C_4H_9CONH)_2PtCl_2]$. The "Platinblau" was also studied by Brown et al., and an analogous formula $[(CH_3CONH)_2Pt(OH)_2]$ was given. Since then, more blue platinum compounds have been synthesized and among them are the platinum pyrimidine blues[6] which show a high index of antitumor activity with a lower associated nephrotoxicity than *cis*-dichlorodiammineplatinum(II) or *cis*-DDP. The platinum pyrimidine blues have been obtained by incubation of various pyrimidines with the hydrolysis product of *cis*-DDP, and they were found to be polymeric and paramagnetic.[7,8] Like other blues, the platinum pyrimidine blues were isolated as amorphous solids and detailed structural information of platinum blues remained elusive until single crystals of *cis*-diammineplatinum α-pyridone blue or PPB were prepared.[9] Extensive studies on PPB were performed to determine the solid-state structure,[10] magnetic properties,[10] X-ray photoelectron spectroscopic properties,[11] and chemical and spectroscopic properties in aqueous solution.[12] All of these studies suggest that at least three properties are shared by most platinum blues in solution and in the solid state: mixed valency, oligomerization, and multidentate ligand bridging (e.g., amidate bridging). The blue color may arise from a mixed-valence or intervalence electronic transition, but no detailed absorption studies have been reported.

In order to make a comparative study about new platinum blues and to understand the origin of the blue color, we have carried out the reactions of *cis*-DDP with saccharate (I) and phthalimide (II). Both ligands are capable of amidate bridging with similar structures. Reactions with *cis*-DDP and saccharate did not give a blue solution nor a blue precipitate. However, the colorless product isolated seems to be an interesting 5-coordinated square-pyramidal platinum species which we will report on later.[13] On the other hand, reactions with *cis*-DDP with the use of phthalimide yielded very intense blue solutions, and blue precipitates were isolated. This paper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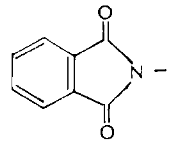
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reports our results on the synthesis and characterization of the platinum phthalimide blues.

Experimental Section

Absorption studies in the UV-visible range were made on a Cary 17 Dx spectrophotometer. Low temperatures were monitored with an Air Products Model Lt-3-110 Heli-Tran system. Liquid nitrogen was used as the refrigerant.

NMR spectra were recorded on a Hitachi-Perkin-Elmer R20-B spectrometer with a FT device and IR spectra (4000–250 cm^{-1}) on a Perkin-Elmer PE-457 IR spectrometer.

Room-temperature magnetic susceptibility measurements were made with a Faraday balance from Cahn Instruments. All of the platinum phthalimide blue samples were diamagnetic.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis. The starting materials, *cis*-$PtI_2(NH_3)_2$ and *cis*-$PtCl_2(NH_3)_2$, were prepared by the literature method, with minor modifications.[14] Potassium phthalimide was purchased from Aldrich Chemical Co. and used without further purification.

In a typical synthetic procedure, 0.30 g of *cis*-$PtI_2(NH_3)_2$ was dissolved in 10 mL of water, and a slight excess of $AgNO_3$ was added to precipitate AgI. The AgI was filtered, and a dilute KCl solution was added to the filtrate to ensure the absence of silver ion. The solution was centrifuged and then filtered. A stoichiometric amount (1:1 or 1:2 Pt-to-ligand mole ratio) of potassium phthalimide solution (~10 mL) was then added to the filtrate. The white precipitate, presumably the square-planar complex which appeared several minutes after the addition of the ligand, was then filtered. To the final filtrate was added ~2 g of $NaNO_3$, and the solution was incubated at 37–40 °C in a water bath and a blue color usually appeared within 24 h. The incubation was continued for a couple of days, and the solution was then cooled to room temperature. A blue precipitate formed upon cooling, and it was collected by filtration. The compound was dried in a desiccator by anhydrous $CaSO_4$. The yield was generally low, in the range of 30–60 mg. If the yellow-brown filtrate was heated to ~60 °C for several hours, a blue solution appeared again and another crop of blue precipitate could be obtained upon cooling the solution.

Oxidative Titration. The oxidative titrations of the platinum blues were monitored potentiometrically with use of platinum vs. calomel reference electrodes.[15] The titrant was Ce(IV), 4.806 × 10^{-3} N in 0.72 N H_2SO_4, which was standardized with use of normal procedures. The titration was checked by use of a known concentration of K_2PtCl_4 in HCl solution. The titrand was prepared by adding about 70 mL of 4.5 M HCl to a solid sample of platinum phthalimide blue (~3 mg). The voltage was obtained by taking a reading 1 min after each addition of the titrant. The average oxidation state per platinum atom was calculated based on the percentage of platinum in the sample. Percent platinum was determined by elemental analysis.

Results and Discussion

Synthesis. The platinum phthalimide blue compounds were prepared by using procedures similar to those used for most other platinum blues.[12,16] The preparation scheme is shown in Figure 1.

Several common characteristics are observed in the preparation of platinum phthalimide blues. First, the solution must be acidic (pH ≤5) to obtain a blue species. The blue compounds are destroyed by adding bases. Second, an anion effect is operative; i.e., in the presence of chloride or iodide ion, only a greenish blue solution is obtained but a dark blue solution appears if the halide ions are removed and nitrate ions are added.[12] Third, the blue species are air stable.

The platinum phthalimide blues are, however, unique in terms of obtaining the solid precipitates. When the blue solutions (after incubation for 1 day) are heated, the blue species coagulate to form polymers and precipitate out. The supernatant then becomes yellow-brown. After the blue precipitate is removed and the filtrate heated, a blue solution is obtained once more and another crop of blue precipitate can be obtained. The cycle in general runs two to three times and then no blue solution can be obtained.

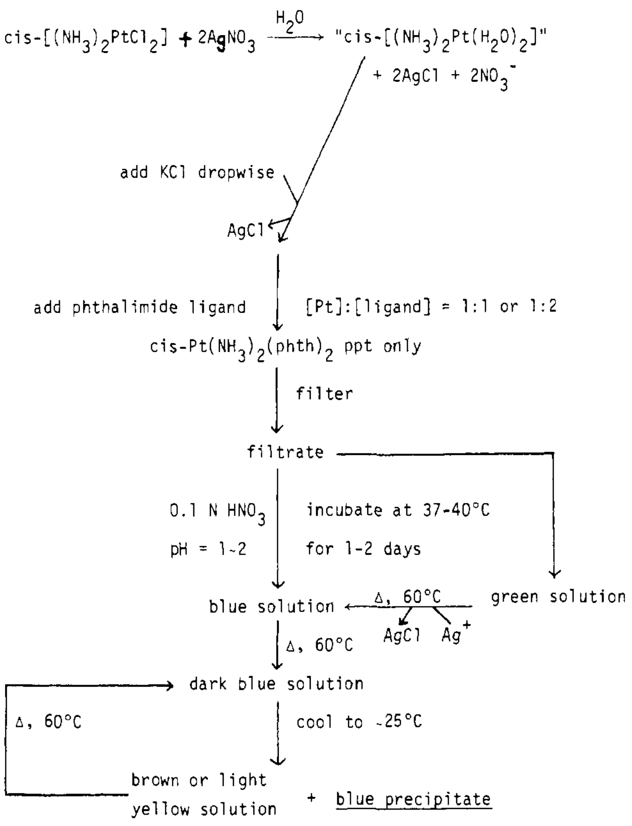

Figure 1. Preparative scheme for platinum phthalimide blues.

In our study, a total of three platinum phthalimide blue compounds were isolated. Two were prepared by using a Pt to ligand mole ratio of 1:2; one is insoluble in water (designated at 1-2A) and the other is slightly soluble in water (designated as 1-2B). The third blue precipitate was obtained by using a Pt to ligand concentration ratio 1:1; it is also insoluble in water (designated as 1-1A). It is highly probable that other slightly different phthalimide blues can be obtained. This phenomena are not unusual for platinum blues; see, e.g., Platinblau.[5,15] Up to the present we have obtained no single crystals.

Before the blue solution was heated and each blue precipitate isolated, the solution absorption spectra were recorded for compounds 1-2A and 1-2B (Figure 2). A symmetrical broad band centered at 590 nm was obtained for 1-2A, and an unsymmetrical broad band centered at 625 nm was obtained for 1-2B. No additional absorption was observed at wavelengths greater than 750 nm in both cases. This may indicate that in solution only one or two species are present initially. If the solutions were heated or allowed to stand for several days, broad-band absorption spectra with more than two peak maxima were obtained. This result is very similar to the spectrum of 1-2B measured in a KBr pellet (Figure 3). This seems to indicate that the formation of insoluble, long-chain platinum phthalimide blue is favored at higher temperatures and concentration. It may be true that because of the low solubility in aqueous solution, the formation of the blue precipitates is irreversible. It should be noted that our rationalization of the observation is not unique because both $[Rh(CNPh)_4]^+$ and $[Ir(CNCH_3)_4]^+$ were found to form face-to-face stacking oligomers according to eq 1.[17,18] The

$$n[M(CNR)_4]^+ \rightleftharpoons [M(CNR_4)]n^{n+} \quad M = \mathrm{Rh\ and\ Ir} \qquad (1)$$

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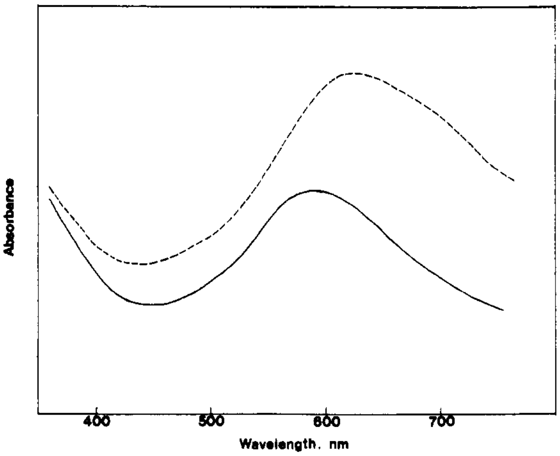

Figure 2. Solution absorption spectra of platinum phthalimide blues: —, 1-2A; ---, 1-2B (for definition see text). The spectra are purposely drawn separately.

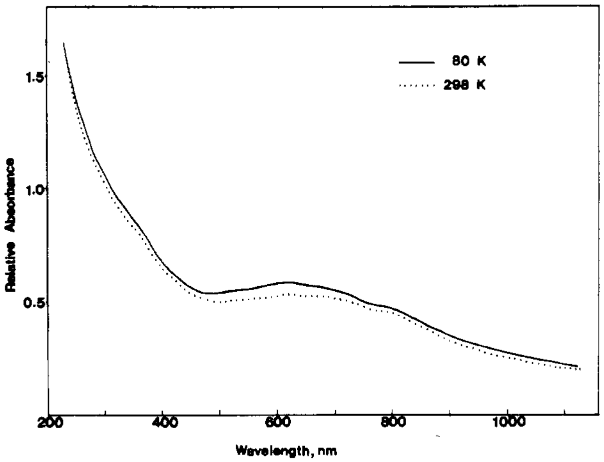

Figure 3. Absorption spectra of platinum phthalimide blue (1-2B) in KBr pellet at 80 and 298 K.

rhodium(I) complex is interesting because equilibrium constants for dimerization and trimerization can be estimated.[19] However, our platinum phthalimide blues are more like the iridium(I) complex for which a high degree of oligomerization in solution was proposed.[18]

The three isolated blue precipitates are all insoluble in most organic solvents. In DMF and Me_2SO, decomposition occurred for all three species. The species are found to be highly positively charged on the basis of their strong adsorption toward the Dowex 50W-X8 cation exchange resin (20–50 mesh, H^+ form).

IR and NMR Spectra. The IR spectrum of 1-2B in a KBr pellet, like many other platinum blues, shows only a broad envelope of bands which are very difficult to assign. The broad band from 3600 to 3200 cm^{-1} apparently is associated with amino group and aromatic carbon–hydrogen stretchings. The broad band centered at 1550 cm^{-1} is related to the amidate carbonyl stretching. A third broad band centered at 1370 cm^{-1} is also observed. Coordinated water, hydroxyl group, and water of hydration are very likely to be present on the basis of IR information. The FT proton NMR spectrum of 1-2B in D_2O shows no peak in the region of 7–8 ppm, indicating that the aromatic protons are missing.

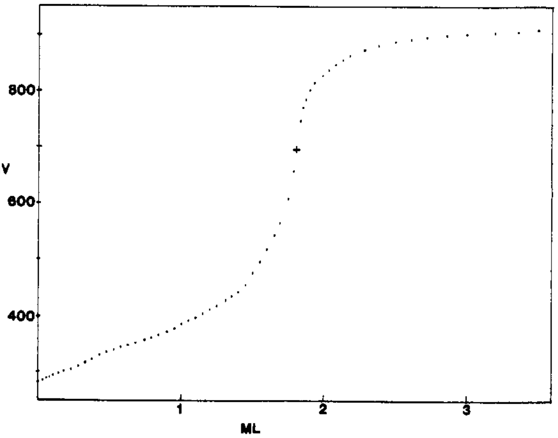

Figure 4. A typical Ce(IV) titration curve for platinum phthalimide blue (1-2A, 3.31 mg); [Ce(IV)] = 4.806 × 10^{-3} M.

Table I. Platinum Oxidation State of Some Platinum Blues

platinum blues	oxidn state of Pt	ref
platinum phthalimide blue (1-1A)	3.3	this work
platinum phthalimide blue (1-2A)	2.9	this work
(1-2B)	3.0	this work
Platinblau	3.01	8
platinum α-pyridone blue	2.25	9

Table II. Elemental Analyses Data of Platinum Phthalimide Blues

compd	% C	% H	% N	% Pt
1-1A	17.14	1.68	9.18	36.23
1-2B	16.78	2.54	9.55	45.36
calcd[a]	16.76	1.98	9.78	45.40

[a] Based on the formula $Pt_4C_{24}H_{44}N_{12}O_{28}$.

Oxidative Titration Data. The potentiometric redox titrations were performed in a similar way as for other platinum blues. All three samples (1-1A, 1-2A, and 1-2B) were titrated in ~5 M HCl solutions with use of Ce(IV) as titrant, and reproducible results were obtained. In each case, only one inflection point was observed (Figure 4). The data were corrected with respect to average oxidation state per platinum atom and are shown in Table I. Also listed in Table I were data obtained from platinum α-pyridone blue and Platinblau. It is interesting to see that 1-2A and 1-2B have roughly +3 oxidation state per platinum and that 1-1A has a higher oxidation state, ~+3.3. We believe that our oxidation state titration results are reasonable because (1) the data are reproducible, (2) there is no change of potential with time, and (3) correct results are obtained for a series of compounds (e.g., platinum α-pyridone blue) whose oxidation state are known.[15]

Elemental Analyses and Proposed Structures. Elemental analyses data have been obtained for samples 1-1A and 1-2B and are given in Table II. We have tried to fit the data to possible structures of the phthalimide blues but have to conclude that a mixture of polymeric species are involved. However, for 1-2B, the basic structure is proposed to be a tetrameric platinum unit (2 Pt(II) and 2 Pt(IV) on the basis of oxidative titration data) with three bridging phthalimide ligands. The sample 1-1A is probably a mixture of polymeric species with a basic structure of Pt(IV)–Pt(II)–Pt(IV) with three phthalimide ligands. On the basis of low nitrogen content, it is highly possible that some of the coordinated ammonia molecules are replaced by water or hydroxyl groups.

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The ligand phthalimide is not likely to bridge three platinum atoms because of the steric constriction imposed on the binding sites.

Mixed-Valence Absorption Spectra and the Nature of Platinum Blues. The deep blue color of platinum blues arises from strong, broad absorptions with maxima in the region of 550–800 nm. The estimated molar absorptivities are generally greater than 500 $\mathrm{cm^{-1}\ M^{-1}}$. This absorption has been attributed to a mixed-valence (MV) transition. In simplest terms, MV transitions arise from electronic transitions between metal centers of different oxidation states. Optical studies have been particularly useful in understanding MV systems. Robin and Day have classified MV compounds into three classes, I, II, and III, depending on the extent of interaction between the two valence states.[20] If the two states are weakly coupled electronically, it is assigned as a localized class II system. On the other hand, a delocalized class III MV compound is electronically strongly coupled. (There is no rigorous quantitative description of these three classes.) Hush has derived several formulas which describe various characteristics of the MV band based on a weak-interaction model[21] which has been very successful in analyzing class II MV systems. One feature of Hush's model is the relation between half-bandwidth (Δ) and position of the MV band (eq 2). The half-bandwidth is

$$\nu_{\mathrm{MV}} = \Delta^2/2310 \qquad T = 300\ \mathrm{K} \tag{2}$$

also related to the vibrational quantum participating in the Franck–Condon process according to eq 3 where $\Delta(T)$ and

$$\Delta(T) = \Delta(0)\ \coth\ (h\nu/2KT)^{1/2} \tag{3}$$

$\Delta(0)$ represent the half-bandwidth of the absorption band at T and 0 K, respectively. The latter value is extrapolated from low temperature measurements. In addition, the valence delocalization parameter (α) which measures the extent of delocalization of valence shell electrons of the two mixed valence centers can be calculated by using eq 4, where $\epsilon_{\max}$ and ν_{MV}

$$\alpha^2 = (4.24 \times 10^{-4})\epsilon_{\max}\Delta/\nu_{\mathrm{MV}}d^2g^2 \tag{4}$$

are the molar extinction coefficient at band maximum and the position of the MV band, respectively, and d and g are the internuclear distance and the difference in oxidation state of the two metal centers, respectively.

In order to test the applicability of the Hush model to platinum blue systems, we have measured the absorption spectra of the platinum phthalimide blue 1-2B in a KBr pellet at various temperatures. Figure 3 shows the spectra obtained at room temperature and 80 K. (The spectrum measured at 164 K simply lies in between the two spectra.) The intensity of the band at 620 nm increases with decreasing temperature which is consistent with an electric dipole-allowed transition.[15] On the other hand, it is interesting to note that contrary to the Hush model (eq 3) the half-bandwidth does not decrease at lower temperature. Similar results have been obtained for some other platinum blues, i.e., platinum α-pyridone blue and Platinblau.[22]

We can use eq 2 to calculate the mixed-valence half-bandwidth for the Figure 2 spectra of the platinum phthalimide blues. If $\nu_{\mathrm{MV}} = 16\,900\ \mathrm{cm^{-1}}$ the calculated half-bandwidth is 6300 $\mathrm{cm^{-1}}$ in comparison with the measured value of ~3900 $\mathrm{cm^{-1}}$. Similar results are obtained for Platinblau and platinum α-pyridone blue samples. The observed sharper half-bandwidth and less experimental temperature-dependence behavior then calculated may indicate strong electronic delocalization.

In order to calculate the valence delocalization parameter α (eq 4), we must know the metal–metal separation, d. For our platinum phthalimide blue samples we have not determined d; thus, we will here use Platinblau data for which we have recently reported[22] an amorphous X-ray determination of the metal–metal separation. The results are the same for solution and for KBr pellets. With the pellet data $\epsilon_{\max} = 1790\ \mathrm{cm^{-1}\ M^{-1}}$, $\Delta = 9190\ \mathrm{cm^{-1}}$, $\nu_{\mathrm{MV}} = 15\,100\ \mathrm{cm^{-1}}$, $d = 2.76$ Å, and $g = 2$, we obtain the result that $\alpha = {\sim}0.12$. This value seems reasonable when compared with two other systems: (1) For several bridged Pt(II)–Pt(IV) halides with Pt–Pt distance of ~5.5 Å, α values are found in the range of 0.03–0.05.[23] (2) For the di-μ-oxo-bridged Mn(III)–Mn(IV) dimer in which the Mn–Mn distance is 2.72 Å, a value of $\alpha = 0.1$ has been calculated.[24] The Hush model has been successful in analyzing the Mn system and the high α value of 0.1 is very likely indicative of a class II–class III borderline case. Similar results ($\alpha \geq 0.1$) are expected for other platinum blues because both X-ray diffraction[22] and EXAFS[25] data indicate short Pt–Pt distances.[26]

In summary, the Hush model has failed to predict the temperature dependence and the half-bandwidth of the MV absorption profiles. However, Beattie, Hush, and Taylor have recently modified the Hush model to account for the relatively sharper absorption bandwidth as delocalization increases.[27] The modification predicts that the MV bandwidth will increase more slowly with temperature as a system becomes more delocalized.[28] This is consistent with our experimental results for platinum blues. Therefore, we feel the *platinum blues are best described as class II–class III borderline or delocalized class III MV compounds.*

The theoretical limitations of Hush's model have been recently discussed by Wong, Piepho, and Schatz[29] in comparison to their newly developed vibronic coupling (PKS) model.[30] According to their analysis, if a mixed-valence system is a class III compound (or when $|\epsilon| > \lambda^2 + W$ for PKS model[30]), Hush's formulas cannot be applied to MV absorption profiles. Although no simple analytical equations have been given by the PKS model for class III MV systems, the PKS model predicts that as delocalization increases to its limit (or $\lambda^2/|\epsilon| \to 0$), negligible temperature dependence will be observed. Further studies using the PKS model for platinum blues should be of primary importance in understanding the electronic spectra. Presently, we are carrying out such model studies for selected platinum blues.

Conclusion

In this paper we have discussed three different aspects of the characterization of the newly prepared platinum phthalimide blues. First, from the synthesis and solution and solid-state absorption studies, the platinum phthalimide blues are

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(26) It should be noted that the situation for platinum α-pyridone blue (PPB) is more complicated than our Platinblau example. For our Platinblau samples in solution or in pellets the oscillator strength of the mixed-valence band is the same, but for PPB the mixed-valence extinction coefficient is a highly sensitive function of the anions present in solution.

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(28) We note here that Wong, Schatz, and Piepho have argued that this modification has no quantitative applicability in the region of the crossover to the localized case ($\lambda^2/|\epsilon| = 1$) and in the delocalized limit ($\lambda^2/|\epsilon| \to 0$).[30]

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found to form insoluble, polymeric species upon heating and concentration. Second, blue compounds with different average platinum oxidation states can be obtained by varying the mole ratio of the starting materials. Third, the mixed-valence absorption profiles at various temperatures are examined with use of Hush's model. Our optical and magnetic results strongly suggest that the platinum phthalimide blues are best described as class II–class III borderline mixed-valence compounds in which there is extensive delocalization but inequivalent metal sites.

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Registry No. *cis*-$PtI_2(NH_3)_2$, 15978-93-5; potassium phthalimide, 1074-82-4; *cis*-DDP, 15663-27-1.

Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry,
Guelph Campus, University of Guelph, Guelph, Ontario, Canada, N1G 2W1

Reactivity of Platinum Diolefin Complexes. Roles of Trans Influence and Chelate Effect

G. K. ANDERSON, H. C. CLARK,* and J. A. DAVIES

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The complex $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene) reacts with CO and tertiary phosphine to produce *cis*-$[PtCl_2(CO)L]$ (L = PEt_3, P-*n*-Bu_3, $PMePh_2$, PPh_3, $P(C_6H_4F\text{-}p)_3$, or $P(c\text{-}Hx)_3$), which have been characterized by infrared and ^{31}P NMR measurements. The reaction was studied by ^{13}C and ^{31}P NMR, infrared and electronic spectroscopies, and possible mechanisms are discussed in terms of the chelate effect of the diolefin. Complexes $[PtR_2(cod)]$ (R = Me or Ph) react with CO to give $[PtR_2(CO)_2]$, while $[PtClR(cod)]$ complexes undergo carbonyl insertion to yield $[PtCl(COR)(cod)]$. Reactions of these species with $PMePh_2$ were also studied. The ^{13}C NMR spectra and reactions of the cyclooctadiene complexes are discussed in terms of the trans influence of the organo ligands and the chelate effect.

Introduction

Transition-metal complexes of weak donor ligands, and in particular platinum and palladium complexes of the type $[MX_2L_2]$ (M = Pd or Pt, X = anionic ligand, L = weak donor ligand), are useful starting materials in organometallic and coordination chemistry. Their usefulness lies in the ease with which the donor ligand may be displaced. While commonly encountered leaving groups include nitriles,[1-3] dialkyl sulfides,[4] and dialkyl sulfoxides,[5,6] chelating diolefins such as norbornadiene, 1,5-cyclooctadiene, and cyclooctatetraene are especially suitable since they maintain a cis configuration about the metal, and their complexes are stable under the conditions required to modify the other groups around the metal center.[7-9] Subsequent displacement of the diolefin to give the desired product is then a very facile process.

An unusual example of such displacement has been noted[10] in the reaction of $[PtCl_2(nbd)]$ (nbd = norbornadiene) with two different incoming nucleophiles, namely, CO and $P(c\text{-}Hx)_3$ or $P(o\text{-}tolyl)_3$ to give *cis*-$[PtCl_2(CO)(PR_3)]$ complexes. This is particularly convenient since the usual route to *cis*-$[PtCl_2(CO)(PR_3)]$ complexes via cleavage by CO of the chloride-bridged complex $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ is not available with these bulky phosphines.

It was therefore decided to extend this reaction to the 1,5-cyclooctadiene complex, $[PtCl_2(cod)]$, to investigate the mechanism of formation of *cis*-$[PtCl_2(CO)L]$ (where L is tertiary phosphine), and to discover whether this type of reaction could be extended to the $[PtClR(cod)]$ and $[PtR_2(cod)]$ (R = Me or Ph) systems.

Experimental Section

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 60.0, 15.1, and 24.3 MHz, respectively, on a Brüker WP-60 spectrometer operating in the FT mode. Spectra were run for $CDCl_3$ solutions at 25 °C (except where stated); ^1H and ^{13}C chemical shifts were measured relative to Me_4Si, and ^{31}P chemical shifts were measured relative to external H_3PO_4, downfield shifts being positive.

Infrared spectra were measured in $CHCl_3$ solution with use of NaCl solution cells of path length 0.1 mm or as Nujol mulls between CsI plates and were recorded on a Perkin-Elmer 180 spectrophotometer.

Electronic spectra were obtained with the use of a Cary 118 spectrophotometer. Measurements were performed upon $CHCl_3$ solutions in 2-cm quartz cells.

Molecular weight determinations were carried out on $CHCl_3$ solutions at 37 °C with the use of a Perkin-Elmer 115 instrument.

Carbon-13 labeled carbonyl complexes were prepared with use of 90% enriched ^{13}CO obtained from Prochem. The complexes $[PtMe_2(cod)]$, $[PtClMe(cod)]$, $[PtPh_2(cod)]$, and $[PtClPh(cod)]$ were prepared by reported methods.[8] The complexes *cis*-$[PtCl_2(CO)(PR_3)]$ were all prepared similarly, so a typical example only is given.

Preparation of *cis*-$[PtCl_2(CO)(PMePh_2)]$. Carbon monoxide was passed through a suspension of $[PtCl_2(cod)]$ (0.226 g, 0.604 mmol) in chloroform (30 mL). After 1 h, a chloroform solution of $PMePh_2$ (0.121 g, 0.604 mmol) was added dropwise over 30 min, and CO passage was continued for a further 30 min. Concentration of the solution and ether addition caused precipitation of white crystals (0.233 g, 78%).

Preparation of $[PtCl(COPh)(cod)]$. Carbon monoxide was passed through a solution of $[PtClPh(cod)]$ (0.395 g, 0.951 mmol) in chloroform (20 mL) for 1 h. The volume of the pale yellow solution was reduced, and the addition of ether caused precipitation of pale

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