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Photochemistry of Dimeric and Trimeric Hydroxo-bridged Diammine Platinum(II) Complexes in Aqueous Solution

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The irradiation of aerated aqueous solutions containing cis-$Pt(NH_3)_2(H_2O)_2^{2+}$ *with 254-nm light gives rise to the formation of a blue product identified as a mixed valence (Pt(II)/Pt(IV) = 2) hydroxo bridged trinuclear cationic complex* $[Pt_3(NH_3)_4(OH)_6]^{2+}$. *The photoreactive species have been identified as the dimeric and trimeric hydroxo bridged platinum compounds that are present in solution and have the maximum concentration at pH 6.5. The reaction is initiated in a OH → Pt charge transfer excited state, to give a primary photoreaction intermediate which undergoes thermal air oxidation to give the final blue product.*

Introduction

After the discovery of the antitumoral activity of *cis*-$Pt(NH_3)_2Cl_2$, platinum complexes have attracted the interest of a great number of researchers in biological as well as in chemical fields. Particular attention has been devoted in recent years to the series of complexes discovered by Rosenberg and Mansy [1] and named 'platinum pyrimidine blues'. Several investigations [2] on the nature and the possible structure of these compounds have been reported; the results obtained indicate: (i) that platinum pyrimidine blues are polynuclear compounds formed through the reaction of the hydrolysis products of *cis*-$Pt(NH_3)_2Cl_2$ with pyrimidine bases, (ii) that they contain platinum in different oxidation states, (iii) that oxidation of Pt(II) to paramagnetic Pt(III) is likely to occur in the formation reaction, (iv) that their characteristic blue color is retained when these compounds are brought into solution, suggesting that *intramolecular* intervalence absorptions are responsible for their blue color.

Before the discovery of platinum pyrimidine blues, other mixed-valence, platinum blue compounds [3] had been synthesized. In contrast with the platinum pyrimidine blue compounds, these compounds lose their characteristic blue color in solution, indicating that *intermolecular* intervalence absorption processes are occurring only in the solid state condition.

Common to all the platinum blues referred to above is the fact that they are formed when Pt(II) complexes are allowed to react with nitrogen-containing organic compounds. The only known completely inorganic platinum blue compounds are those which are obtained by U.V. irradiation of platinum(II) diammine complexes. Several years ago, Babaeva and Motiagina [4] reported on the formation of a blue mixed valence (Pt(II)–Pt(IV)) compound upon U.V. irradiation of *cis*-$Pt(NH_3)_2Cl_2$ in aqueous solution; the authors proposed for this product a hydroxo bridged tetrameric structure with Cl and OH ligands coordinated to platinum centers. The formation of a blue compound was obtained recently [5] by X-ray irradiation of solid $[Pt_2(NH_3)_4(OH)_2](NO_3)_2$ dimeric species; a molecular mechanism which implies the oxidation of Pt(II) to Pt(IV) by oxygen atoms formed in the initial photolysis of NO_3^- was proposed. The final product was formulated as a dimeric 'mixed valence chromophore' containing hydroxo bridged platinum(II) and platinum(IV) species. In a recent paper [6] we have reported some preliminary results on the formation of a blue platinum compound upon U.V. irradiation of [*cis*-$Pt(NH_3)_2(H_2O)_2]SO_4$ in aqueous solution. The reaction product was identified as a mixed valence (Pt(II)/Pt(IV) = 2) hydroxo bridged trinuclear cationic complex; also, experimental evidence suggested that the hydroxo bridged trimeric species, which is known to be present in aqeuous solution of *cis*-platinum aquo complexes [7, 8], is responsible for the observed photochemical behavior.

In the present study the photochemical behavior of solutions of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ is examined in some detail with the aim of obtaining additional evidence regarding the molecular structure of the blue platinum product, the mechanism of its formation, and the nature of the photoreactive species.

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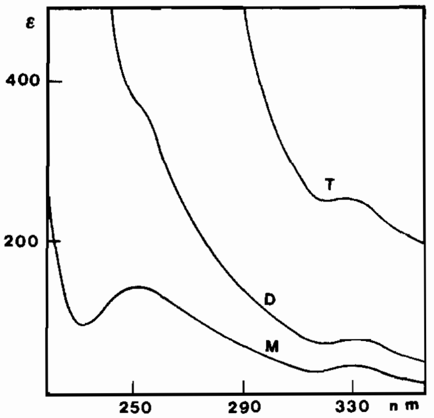


Fig. 1. Absorption spectra of aqueous solutions of [*cis*-$Pt(NH_3)_2(H_2O)_2](ClO_4)_2$ at pH < 2 (M); $[Pt_2(NH_3)_4(OH)_2](ClO_4)_2$ at pH 6.5 (natural pH) (D); $[Pt_3(NH_3)_6(OH)_3]_2(SO_4)_3$ at pH 6.5 (natural pH) (T).

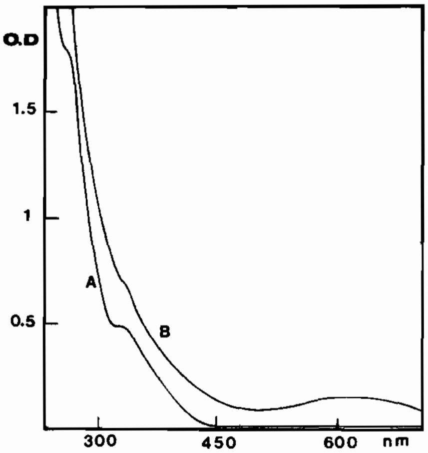


Fig. 2. Spectral variations observed during the irradiation of a 1.1 × 10^{-2} *M* solution of [*cis*-$Pt(NH_3)_2(H_2O)_2](ClO_4)_2$ at initial pH 3.5; A, before irradiation; B, after 120 minutes of 254-nm irradiation.

Experimental

Materials

cis-dichlorodiammineplatinum(II) was prepared according to reference [9] from K_2PtCl_4(BDH).

Aqueous solutions of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ were obtained from *cis*-$Pt(NH_3)_2Cl_2$ by using stoichiometric amounts of Ag_2SO_4 or $AgClO_4$ as precipitating agents. The concentrations of the solutions were always checked by measurements of the total platinum concentrations by the atomic absorption spectrophotometric technique, and were in excellent agreement with those expected on stoichiometric grounds.

Cyclo-tri-μ-hydroxo-tris[*cis*-diammineplatinum-(II)] sulphate hexahydrate (trimer sulphate) was prepared from 6.85 × 10^{-2} *M* solutions of [*cis*-Pt-$(NH_3)_2(H_2O)_2]SO_4$ according to reference [8]. In the preparation of this compound some di-μ-hydroxo-bis[diammineplatinum(II)] sulphate (dimer sulphate) was obtained in the first crop; it was separated from the more soluble trimer compound by crystallization. The purity of the solid trimer sulphate was checked by I.R. spectroscopy.

Di-μ-hydroxo-bis[diammineplatinum(II)] perchlorate (dimer perchlorate) was prepared from a solution of [*cis*-$Pt(NH_3)_2(H_2O)_2](ClO_4)_2$ following the procedure described in reference [10] for the di-μ-hydroxo-bis[diammineplatinum(II)] nitrate. The I.R. spectrum of the pale yellow crystals obtained was in good agreement with that previously reported for the dimer nitrate [10], indicating that contrary to the nitrate case, formation of trimer perchlorate is negligible.

The dimer sulphate was easily obtained by adding some drops of a saturated solution of Na_2SO_4 to a solution of dimer perchlorate. The precipitated crystals were washed with water, ethanol, and then dried under rotary pump vacuum for several hours. This procedure was found to give much better yield than a previously reported one [8].

All the other chemicals used were Fluka products of reagent grade.

Apparatus and Methods

pH measurements were performed with a Beckman Select Ion 5000 ion analyzer using a standard combination electrode.

UV–VIS spectra were recorded with a Varian Cary 219 spectrophotometer.

I.R. spectra were recorded with a Perkin-Elmer mod. 283 spectrophotometer using KBr pellets.

The irradiation equipment was the same as previously described [11]. The solutions were deoxygenated before irradiation by freeze–pump–thaw method.

Atomic absorption measurements were performed with a Perkin-Elmer mod. 603 atomic absorption spectrophotometer.

Results

It is well known [7, 8, 10] that aqueous solutions of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ contain dimeric and/or trimeric species in equilibrium with the monomer, the relative concentration being dependent on pH. The absorption spectra of the three compounds are shown in Fig. 1. It should be noticed that the spectrum of the monomer was obtained from an aqueous solution of the bis-aquo complex kept at pH lower than 2; namely, in conditions where the concentrations of oligomeric species are quite negligible.

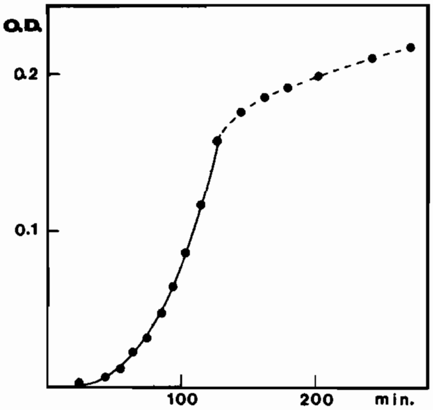


Fig. 3. Absorbance variations observed at 630 nm for a 1.1 × 10^{-2} *M* aqueous solution of [*cis*-$Pt(NH_3)_2(H_2O)_2$]-$(ClO_4)_2$ at initial pH 3.5; full line, under 254-nm irradiation; dashed line, in the dark after irradiation.

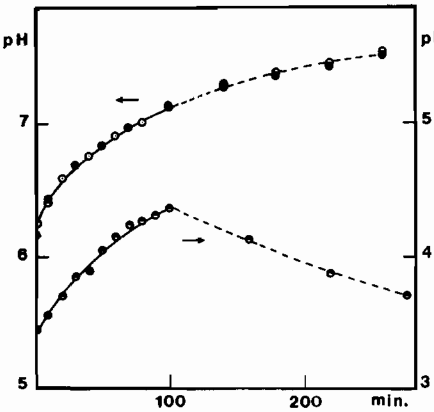


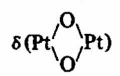
Fig. 4. pH variations observed for 1.1 × 10^{-2} *M* aqueous solutions of [*cis*-$Pt(NH_3)_2(H_2O)_2$]$(ClO_4)_2$ (◐); [$Pt_2(NH_3)_4$-$(OH)_2$]$(ClO_4)_2$ (●); [$Pt_3(NH_3)_6(OH)_3$]$_2(SO_4)_3$ (○); full line, under 254-nm irradiation; dashed line, in the dark after irradiation.

Irradiation with 254-nm light was performed on aged aqueous solutions of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ at various pH values as well as on aqueous solutions of the dimer and trimer. The results can be summarized as follows.

[cis-*Pt(NH*$_3$*)*$_2$*(H*$_2$*O)*$_2$*](ClO*$_4$*)*$_2$*, pH = 3.5*

The irradiation led to the spectral variations shown in Fig. 2. The increase in the intensity of the broad absorption band centered at 630 nm was responsible for the blue color developing in the irradiated solutions. In contrast with what was previously reported [6] for the irradiation of [*cis*-$Pt(NH_3)_2(H_2O)_2$]SO_4 solutions, in this case no precipitate was observed to form even for long irradiation periods. This allowed the formation of the blue product to be monitored by spectrophotometric means. The absorbance variations observed at 630 nm during and after irradiation are shown in Fig. 3. It should be noted that (i) the formation of the blue product goes on also after the light is switched off; (ii) the reaction rate increases under irradiation.

TABLE I. Infrared Bands of the Blue Product as Sulphate Salt.[a]

cm^{-1}	IR intensity	Assignment
3560···3360[b]	vs[c]	ν(OH)
3260···3140	vs	ν(NH)
2340	vw	$\delta_s(NH_3) + \delta$(PtO–H)
1660	w	$\delta_d(NH_3)$
1640···1550	s	$\delta_d(NH_3)$
1320	vs	$\delta_s(NH_3)$
1160···1100	vs	$\nu_3(SO_4)$
1035	sh	δ(PtO–H)
980	w	$\nu_1(SO_4)$
850···770	m	$\rho(NH_3)$
616	vs	$\nu_4(SO_4)$
550···520	m	ν(Pt–N), ν(Pt–O)
265	w	
250	w	δ(N–Pt–N)

[a] In KBr pellets. [b] Dots between wavenumbers mean multiple, badly resolved maxima. [c] Key: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; vw, very weak.

The pH of the solution increased during the irradiation and decreased in the dark when the irradiation was stopped (Fig. 4).

[Pt$_2$*(NH*$_3$*)*$_4$*(OH)*$_2$*](ClO*$_4$*)*$_2$ *(Dimer perchlorate), pH 6.5 (Natural pH)*

The irradiation of an aqueous solution of the dimer perchlorate gave rise to spectral variations identical to those shown in Fig. 2 for [*cis*-$Pt(NH_3)_2$-$(H_2O)_2$]$(ClO_4)_2$. The formation of the blue compound was observed both during and after the irradiation with a kinetic behaviour similar to that of Fig. 3*.

The pH increased with irradiation, similarly to what happens for *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ at pH 3.5. However, contrary to the previous case when the irradiation was stopped the pH continued to increase (Fig. 4). A qualitatively identical behavior was

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*In a preliminary communication we reported that aqueous solutions of dimer sulphate were inactive in giving the blue product. The discrepancy between that claim and the present results is only due to the previous use of an impure dimer sample, and not to the change in the anion.

observed by using aged solutions of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ at pH 6.5 instead of the dimer.

[cis-$Pt(NH_3)_2(H_2O)_2](ClO_4)_2$ (Monomer perchlorate), pH <2.5

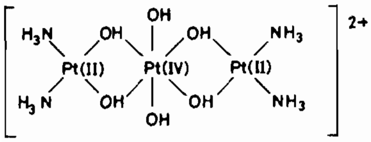
No appreciable reaction was observed even for long irradiation periods. It should be noticed that the blue product obtained at high pH is stable at pH > 2 and decomposes very slowly at lower pH.

The solid blue product was obtained as sulphate salt from irradiated perchlorate solutions by addition of Na_2SO_4 saturated solution. All the blue compounds obtained in the above described conditions showed identical I.R. spectra. The principal I.R. bands are reported in Table I.

As previously reported [6] the formation of the blue product was observed to be strongly oxygen dependent; the irradiation in the absence of air did not give rise to the formation of the blue product. However, if oxygen was allowed to bubble into the solution after the irradiation the blue product was observed to form.

Discussion

The following molecular structure



based on the elemental analysis data and redox qualitative and quantitative tests, was previously proposed [6] for the solid blue product formed by irradiation of aqueous [*cis*-$Pt(NH_3)_2(H_2O)_2]SO_4$.

The I.R. results reported in Table I are in good agreement with this structure; in particular, the absorption at 265 cm^{-1} (which can be assigned to the Pt–O–Pt bend deformation on the basis of that observed at 270 cm^{-1} in the di-μ-hydroxo-bis(diammineplatinum(II) compound [5]) confirms the presence of OH bridges between the platinum atoms.

The intense color of the solid 'blue' sulphate was previously [6] attributed to intervalence transfer absorptions. The blue compound retains its color in solution when it is formed as perchlorate salt; this is an indication that the blue chromophore is a definite molecular species.

The experimental results indicate that dimeric and trimeric species are the reactive species responsible for the photochemical formation of the blue compound. This conclusion is based on the following results; (i) for solutions of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ at pH < 2, where the oligomer concentration is negligible, no reaction is observed; (ii) in aged solutions of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ at pH > 3.5 in which the concentration of oligomers becomes appreciable, photochemical formation of the blue product is observed; (iii) the irradiation of aqueous solutions of the oligomers gives rise to efficient formation of a blue compound which is identical to that observed for monomer solutions (case ii).

Although the predominant role of the oligomers in this photoreaction is no doubt related to their strongest absorption at 254 nm (*vide infra*), this result emphasizes the importance of the previous oligomers in aqueous solutions of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$. This fact should also be taken into consideration when dealing with the mechanism of thermal formation of platinum blues.

The spectral variations (Fig. 2) suggest that the excited oligomers give rise to the formation of an intermediate from which the final product is formed through one or more secondary thermal steps:

$$D \xrightarrow{h\nu} D^* \rightarrow I \rightarrow \cdots\cdot \rightarrow \text{Blue product}$$

The experimental results obtained until now do not allow a characterization of intermediate I. On the basis of the observed influence of oxygen on the reaction it is clear that the secondary thermal steps involve air oxidation processes triggered by the intermediate. Thus, the intermediate is likely to contain platinum in some easily oxidizable form.

As far as the nature of the primary photochemical process is concerned, it does not seem likely that any purely ligand photosubstitution process (*i.e.*, one leaving platinum in its 2+ oxidation state) can produce an air oxidizable intermediate*. Intramolecular photoredox processes producing either platinum(I) or platinum(III) appear to be more likely candidates from this point of view. However, direct formation of platinum(III) in a primary process seems to be quite unlikely in view of the lack of low-energy metal-to-ligand charge transfer (MLCT) states in this complex. On the other hand, formation of platinum(II) species can probably be achieved by homolytic bond splitting in a ligand-to-metal charge transfer (LMCT) state of these complexes. The fact that the photoreaction only occurs with oligomeric species which have intense LMCT transitions (presumably of the OH → Pt type) at the wavelength of excitation seems to support this hypothesis. Thus, we propose that the photochemical blue formation is initiated by a primary process which can be sketched (in the dimer case) as follows:

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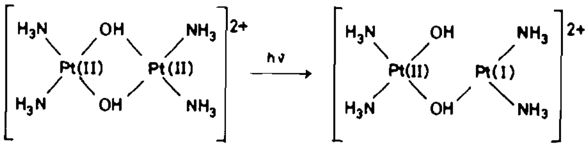
*In fact, all the bis-ammine complexes known are air stable and so are also other aquated platinum(II) species including the tetra-aquaplatinum(II) ion [12].



An elucidation of the secondary (presumably complicated) sequence of events which lead in the presence of oxygen to the formation of the blue product is beyond our capabilities. It can only be noticed that, given the proposed structure of the blue product [6], two ammonia molecules have to be released in these processes for each molecule of blue formed*. This process is likely to be the one responsible for the observed increase in pH accompanying the formation of the blue from the oligomers. The fact that in the aged monomer case the pH decreases in the dark after irradiation is most probably the consequence of the oligomerization processes [14] which take place in order to compensate for the photochemical consumption of the oligomers.

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*Interestingly enough, no photochemical formation of blue products can be observed using oligomerized solutions of Pt(en)$(H_2O)_2^{2+}$ [13].

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