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PHOTOCHEMICAL REDUCTION AND AIR OXIDATION OF cis-DIAMMINEPLATINUM α-PYRROLIDONE TAN IN AQUEOUS SOLUTION

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cis-Diammineplatinum α-pyrrolidone tan cation, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$, is proved to be reduced to dark blue $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$ and yellow $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{4+}$ by water and be oxidized by air to a yellow species of Pt(Ⅲ). The reduction reaction is accelerated by visible light irradiation. Both the reduction and oxidation reactions are completely reversible and the addition of Ce^{4+} or Fe^{2+} quantitatively restores the original species, respectively.

Recently the author has reported on the isolations and crystal structures of a series of mixed-valent tetrameric platinum compounds called under a generic name "platinum blues".1-3) From the studies of several platinum-blue related compounds containing α-pyridone4-7) or α-pyrrolidone,1-3) it was found that the compounds consist of cations with a general formula of $[Pt_4(NH_3)_8L_4]^{n+}$, where L is deprotonated α-pyridone or α-pyrrolidone and n is 4, 5, or 6. The average platinum oxidation state is therefore 2.0, 2.25, and 2.5, corresponding to n = 4, 5, and 6, respectively.

Although salts with these cations have been isolated as crystalline solid, their redox reactions in a solution have not yet been fully studied. Barton et al. reported that cis-diammineplatinum α-pyridone blue cation, $[Pt_4(NH_3)_8(C_5H_4NO)_4]^{5+}$, is decomposed in an aqueous solution on long standing or by oxidation with Ce^{4+}, based on ESR and visible absorption spectral changes.6) However, we have recently noticed that in cis-diammineplatinum α-pyrrolidone tan, $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ (**1**), the cation is reversibly reduced to blue $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$ (**2**) and yellow $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{4+}$ (**3**) on dissolution in water. What is more interesting, the reduction reaction is accelerated by visible light irradiation.

Although dark brownish red compound **1** with average platinum oxidation state of 2.5 is diamagnetic in the solid state,2) the aqueous solution is green and is paramagnetic. The ESR spectrum at -162 °C is characterized by an axial signal, $g_\perp = 2.61$ and $g_\parallel = 1.972$ with approximately nine-line hyperfine splitting, which is basically the same as that reported for cis-diammineplatinum α-pyridone blue6) and is indicative of the existence of one unpaired spin delocalized over four ^{195}Pt nuclei (I = 1/2, 33.7% natural abundance). From the ESR spectrum and the solution color, which resembles to that of recently reported crystals of cis-diammineplatinum α-pyrrolidone green, $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_{5.48}\cdot 3H_2O$, with average platinum oxidation state of 2.37,3) we inferred that some reduction reaction may have occurred in the solution. After repeated attempts to stabilize 1 in an aqueous solution, the author found that it is stable for an appreciably long time in a strongly acidic solution in the dark. However, the color change from tan to green proceeds increasingly rapidly with decreasing acid concentrations and visible light irradiation. When 1 was dissolved in neutral water, the color change was instantaneous and the solution became green. On the other hand, when 1 was dissolved in 1.8 M H_2SO_4 in the dark (1 M = 1 mol dm^{-3}), the solution remained dark red for more than half an hour. If the solution was degassed, the color change was accelerated but the dark red color still remained unchanged for a few minutes. However, when 1 was dissolved in 1.8 M H_2SO_4, with the solution either degassed or not and irradiated with a 300 W tungsten lamp filtered with a Pyrex glass, the solution turned faint green within a minute. The color change in 4.5 M H_2SO_4 is shown in Fig. 1. As the absorption at 478 nm ($\varepsilon = 6.2 \times 10^4$ $cm^{-1}mol^{-1}$ dm^3) decreased, absorption at 680 nm slightly increased with an isosbestic point observed at 598 nm. However, after 10 min, absorption at 680 nm also started decreasing. As a result, the solution gradually turned blue-green. Figure 2 shows how the initially green aqueous solution turned yellow with light irradiation. The color change was by far slow compared to that from tan to green. If the solution was not irradiated, it remained green for at least several hours and then gradually changed to be yellow. These green or yellow solutions could be turned to tan by the addition of Ce^{4+} or $Na_2S_2O_8$, the visible spectra being quantitatively restored. Table 1 summarizes

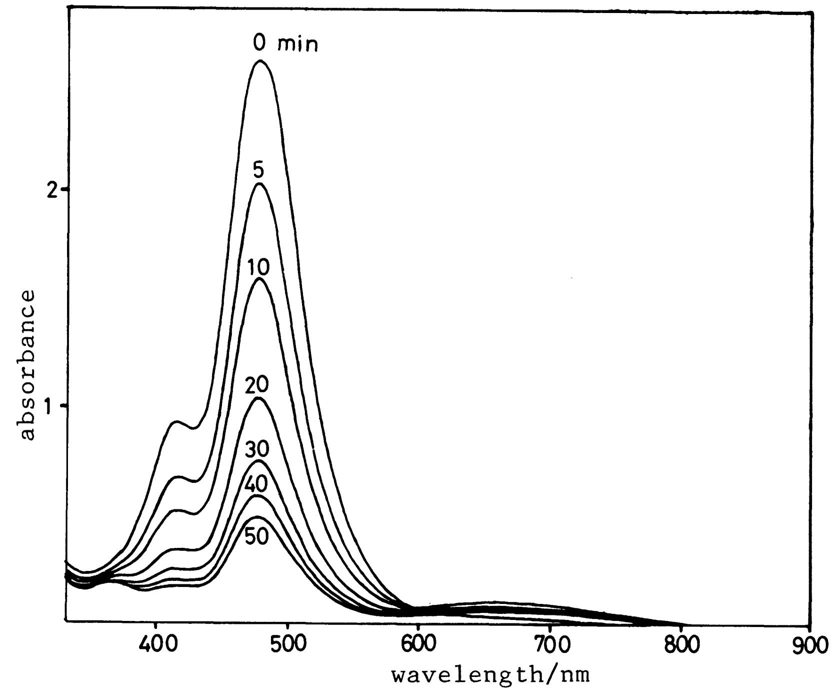

Fig. 1. Spectral change of cis-diammineplatinum α-pyrrolidone tan cation, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$, in 4.5 M H_2SO_4, irradiated with 478 nm light (4.3×10^{-5} M in Ar atmosphere) (1 M = 1 mol dm^{-3}).

the results of the potentiometric oxidative titrations2) of 1 using Ce^{4+} in various acid solutions with different colors. Table 1 shows that, in an inert atmosphere, the platinum is reduced from the oxidation state of 2.5 to 2.25 and 2.0 on dissolution in water, corresponding to the color change from tan to green and yellow. Also interesting is that, if an acidic solution was allowed to stand in air for a few days, the solution turned yellow, where platinum was oxidized to 3.0. This oxidation took place even in the dark and the oxidized yellow species could be reduced to tan or green quantitatively by the addition of Fe^{2+}. It seems that 2 and presumably also 1 are reduced by water, since no color change is observed in DMF or DMSO solutions of dark blue $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_3(NO_3)_2 \cdot 5H_2O$ or violet $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_2(NO_3)_{2.56} \cdot 5H_2O$8) in an inert atmosphere. The former compound was prepared in the same way as that for 1, except that crystallization was carried out in an inert atmosphere with the addition of $NaPF_6$. Further detailed work is now under way and will be published later.

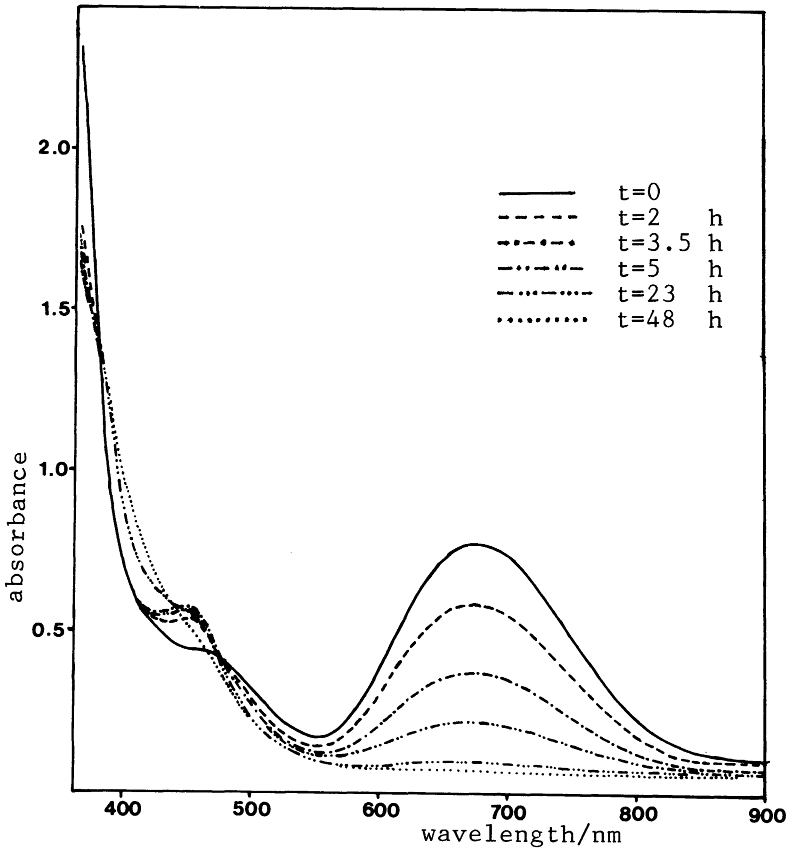

Fig. 2. Spectral change of cis-diammineplatinum α-pyrrolidone tan cation, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$, in an aqueous solution, irradiated with a 300 W tungsten lamp filtered with Pyrex glass (1.4×10^{-3} M in Ar atmosphere) (1 M = 1 mol dm^{-3}).

Table 1. Potentiometric Oxidative Titrations of cis-Diammineplatinum α-Pyrrolidone Tan with Ce^{4+}

Medium	Atmosphere	Time after dissolution	Color	Average Pt ox. state
H_2Oa)	Ar	immediately	green	2.25 ± 0.02

Table 1. (continued)

H_2O[a)]	air	immediately	green	2.30 ± 0.03
H_2O[a)]	Ar	1 week	yellow	1.99 ± 0.02
0.06 M[b)] H_2SO_4	Ar	immediately	green	2.26 ± 0.02
0.06 M[b)] H_2SO_4	air	immediately	green	2.30 ± 0.03
0.06 M[b)] H_2SO_4	air	4 days	yellow	≈ 2.7[c)]
0.06 M[b)] H_2SO_4	Ar	4 days	yellow	2.02 ± 0.02
9 M[b)] H_2SO_4	air	2 days	yellow	≈ 2.9[c)]

a) The solution was acidified to 0.06 M H_2SO_4 before titration.

b) 1 M = 1 mol dm^{-3}.

c) The potential was slightly increasing, which indicates air oxidation was still proceeding.

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