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Redox disproportionation cleavage of an α-pyrrolidonate-bridged mixed-valent tetranuclear platinum complex

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Abstract

The solution properties of α-pyrrolidonate-bridged dinuclear and tetranuclear platinum complexes are described. The general formula of the compounds is $[Pt_2(NH_3)_4(C_4H_6NO)_2]_n^{m+}$, where C_4H_6NO = deprotonated α-pyrrolidone, $n=1$ or 2, $m=2$–4 per dimer unit. The charge m depends on the average Pt oxidation state in the range 2.0–3.0 (the complex takes the four oxidation states Pt^{II}_2, $Pt^{II}_3Pt^{III}$, $Pt^{II}_2Pt^{III}_2$, and Pt^{III}_2). The behavior of the mixed-valent tetranuclear platinum complex $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ ($n=2, m=6$) in aqueous media was investigated by means of UV–Vis and ^1H NMR spectroscopy. It was shown that $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ undergoes a rapid disproportionation cleavage into the dinuclear complexes $[Pt^{II}_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ ($n=1$, $m=2$) and $[Pt^{III}_2(NH_3)_4(C_4H_6NO)_2LL']^{4+}$ ($n=1$, $m=4$; L, L′ are axial ligands). It was also found that the reaction is a reversible process and the equilibrium is largely shifted to the side of the dimers. A ^1H NMR study on the solution of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ confirms the formation of the two dimers in the molar ratio of c. 1:1 An equilibrium study on the axial ligand substitution of $[Pt^{III}_2(NH_3)_4(C_4H_6NO)_2(H_2O)_2]^{4+}$ shows the existence of three different chemical species, diaqua-, aqua-sulfato- and disulfato-coordinated Pt^{III}_2 dimers, in aqueous sulfuric acid solution. The study also confirms that the disproportionation cleavage of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ in aqueous sulfuric acid solution produces these Pt^{III}_2 dimers.

Introduction

In the last decade, great progress has been made in the area of platinum blues and related complexes prepared from the reactions of hydrolysis products of *cis*-$Pt(NH_3)_2Cl_2$ (*cis*-$[Pt(NH_3)_2(OH_2)_2]^{2+}$) with various amides, such as α-pyridone [1, 2], 1-methylthymine [3], 1-methyluracil [2], α-pyrrolidone [4–6] and acetamide [7, 8]. Although the crystal structures of various dinuclear and tetranuclear platinum complexes have been determined by X-ray diffraction techniques, relatively little is known about the solution chemistry of the complexes. In our previous study on the catalytic activity of the α-pyrrolidone complex in the photoreduction of water to hydrogen [9], we have suggested that in aqueous media the $Pt^{II}_2Pt^{III}_2$ tetramer ($[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$) disproportionates into $[Pt^{III}_2(NH_3)_4(C_4H_6NO)_2]_2^{8+}$ [10] and $[Pt^{II}_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ according to reaction (1).

$$2[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+} \rightleftharpoons [Pt^{III}_2(NH_3)_4(C_4H_6NO)_2]_2^{8+} + 2[Pt^{II}_2(NH_3)_4(C_4H_6NO)_2]^{2+} \qquad (1)$$

However, there has been no direct evidence for the nuclearities of the disproportionation products in the Pt^{III} oxidation state. In the present study, we have found that the reaction is rather attributable to a disproportionation cleavage of the $Pt^{II}_2Pt^{III}_2$ tetramer into the Pt^{II}_2 and Pt^{III}_2 dimers as shown in reaction (2).

$$[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+} + L + L' \xrightleftharpoons{K_{disp}} [Pt^{III}_2(NH_3)_4(C_4H_6NO)_2LL']^{4+} + [Pt^{II}_2(NH_3)_4(C_4H_6NO)_2]^{2+} \qquad (2)$$

We report here the details of the reaction, together with a study on the axial ligand substitution reactions of the Pt^{III}_2 dimer, $[Pt^{III}_2(NH_3)_4(C_4H_6NO)_2LL']^{n+}$ (L, L′ = H_2O, OH^- or SO_4^{2-}; $n = 4 - |\text{total charge of LL}'|$).

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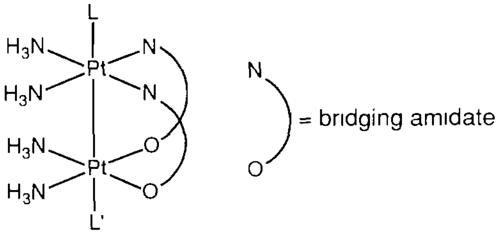
It should be noted here that all the compounds described in the present work are fundamentally composed of dimeric units in a head-to-head arrangement (the amidates bridge in the same direction, as shown below) and the two axial coordination sites of the Pt^{III}_2 dimer are chemically non-equivalent.



Experimental

cis-$Pt(NH_3)_2Cl_2$ (N.E. Chemcat) was used as received. Reagent grade α-pyrrolidone (Tokyo Kasei) was purchased and was purified by distillation before use. Other reagents (reagent grade) used in the syntheses were used as received. Trace analytical grade sulfuric acid (99.7–99.8%, Kanto) and perchloric acid (60–62%, Kanto) were used without further purification. Other reagents used in the measurements were purchased in reagent grade quality and were recrystallized twice from water before use.

The $Pt^{II}_2Pt^{III}_2$ tetramer, $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2(NO_3)_6 \cdot 2H_2O$, was synthesized as previously described [4] with minor modification as follows. A suspension of *cis*-$Pt(NH_3)_2Cl_2$ (1mmol, 0.30 g) and $AgNO_3$ (2 mmol, 0.34 g) in 7 ml of water was vigorously stirred in the dark at 60 °C for 2 h and was kept stirring at room temperature overnight. The white precipitate of AgCl was completely removed either by centrifugation or by filtration. To the filtrate was added α-pyrrolidone (1 mmol, 0.085 ml) and the pH of the solution was adjusted to 4.1–4.2 with 0.5 M NaOH. The solution was heated at 80 °C for 4.5 h under air in the dark. The resulting blue solution was cooled to room temperature and was filtered with a G4 glass filter. Sodium nitrate (0.83 g) and conc. nitric acid (0.2 ml) were then added to the filtrate. The solution was finally bubbled with oxygen gas for *c*. 15 min, until the color of the solution turned to green, and the solution was left at 5 °C for 2 days to form dark red needles of the complex. The crystals were collected by filtration and were dried in a desiccator over silica gel (yield 20–30%). The product was identified by the elemental analysis.

Complex $[Pt^{III}_2(NH_3)_4(C_4H_6NO)_2(NO_3)(OH_2)](NO_3)_3$ was synthesized as follows. To 0.5 ml of 0.01 M $HClO_4$, first 4.9 mg (1.8×10^{-5} mol) of $K_2S_2O_8$ and then 20 mg (1.2×10^{-5} mol) of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2(NO_3)_6 \cdot 2H_2O$ were added. The solution was warmed for a few minutes on a water bath (60 °C) until the color of the solution turned to yellow. After the solution was cooled to room temperature, conc. nitric acid (2.0 ml) was added. The solution was left at 5 °C and was gradually concentrated until orange microcrystals of the complex precipitated. The crystals were collected by filtration and were dried in a desiccator over silica gel (yield 10%). *Anal.* Calc. for $Pt_2O_{15}N_{10}C_8H_{26}$: H, 2.94; C, 10.77; N, 15.69. Found: H, 2.87; C, 10.87; N, 15.75%. UV spectrum (H_2O, 20 °C): $\lambda_{max} = 257$ nm ($\epsilon_{257} = 1.2 \times 10^4$ M^{-1} cm^{-1}); $\lambda_{sh} = 350$ nm ($\epsilon_{350} = 1.8 \times 10^3$ M^{-1} cm^{-1}). Although we have not obtained any evidence for the axial ligands in the proposed formula, it seems probable that the N_4- and N_2O_2-coordinated Pt^{III} atoms are capped by nitrate and aqua ligands, respectively, as in the case of the α-pyridonate-bridged orange crystal, $[Pt^{III}_2(NH_3)_4(C_5H_4NO)_2(NO_3)(OH_2)](NO_3)_3 \cdot 2H_2O$ [11]. The obtained compound was not directly used in the present work but was used in the identification of the Pt^{III}_2 dimer stock solution prepared by mixing equimolar $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2(NO_3)_6 \cdot 2H_2O$ and $K_2S_2O_8$ in H_2O. This stock solution was used to prepare sample solutions in the equilibrium study on the axial ligand substitution reaction of the Pt^{III}_2 dimer.

The hydrogen and sulfate ion concentrations were calculated by using the second dissociation constants of sulfuric acid, 0.0636 (25 °C, $I = 0.75$ M) and 0.102 M (15 °C, $I = 0.90$ M), determined from the literature values [12, 13] by using the Debye–Huckel equation [14]. UV–Vis spectra were recorded on Shimadzu UV-260 and Hitachi 340 spectrophotometers. The temperature of the sample solutions was controlled within ±0.1 °C. ^1H NMR spectra were acquired on a JEOL JNM-GX270 spectrometer in D_2O and were referenced to internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DDS).

Results and discussion

As previously reported [9], the absorption band of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ at 478 nm shows a decrease in absorbance after dissolution of the complex into aqueous solutions (Fig. 1(a)), while the band at 286 nm shows an increase in absorbance. We have also reported that the latter band is also observed for the solution prepared by the persulfate oxidation of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ [9], in which we suggested that the oxidation product might be tetranuclear $[Pt^{III}_2(NH_3)_4(C_4H_6NO)_2]_2^{8+}$ [10]. Since $[Pt^{II}_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ does not show any absorption in the UV–Vis range at wavelengths longer than 240 nm [9], the formation of the complex in the above

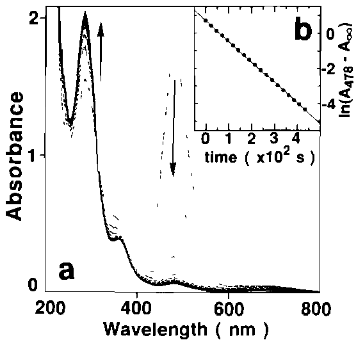


Fig. 1. (a) The time course of UV–Vis spectra. $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2(NO_3)_6 \cdot 2H_2O$ (0.1 mM) was dissolved in 2.03 M H_2SO_4 at 25 °C in air. The spectrum was recorded every 2 min after dissolution. (b) Plot of $\ln(A_{478}-A_\infty)$, estimated from the decrease in absorbance at 478 nm after dissolution of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2(NO_3)_6 \cdot 2H_2O$ (0.1 mM) in 0.254 M H_2SO_4 at 23 °C in air. The solid line is a calculated line according to $\ln(A_{478}-A_\infty) = -k_{obs}t - \ln(A_0-A_\infty)$.

solution could not be confirmed by the spectrophotometric method. However, the existence of the dimer, $[Pt^{II}_2(NH_3)_4(C_4H_6NO)_2]^{2+}$, in the solution could be confirmed with the use of ^1H NMR spectroscopy as described later. It is known that $[Pt^{II}_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ is dinuclear in aqueous media and dimerizes into the $[Pt^{II}_2(NH_3)_4(C_4H_6NO)_2]_2^{4+}$ cation in the solid state [15], in which the interdimer interaction is stabilized by the hydrogen bondings between the oxygen and nitrogen atoms of amidates and ammines. It should be noted here that the formation of $[Pt_2(NH_3)_4(C_4H_6NO)_2]_2^{5+}$ ($n=2$, $m=5$; the formal Pt oxidation state is $Pt^{II}_3Pt^{III}$) can be observed as a band at 680 nm as a side reaction but with minor contribution to the total reaction (Fig. 1(a)).

It was found that the decrease in absorbance at 478 nm obeys a first-order decay (Fig. 1(b)) according to eqn. (3) and that the observed rate constant is

$$A_{478} = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t) \tag{3}$$

independent of the concentration of dissolved $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$, indicating that the reaction is not a bimolecular (eqn. (1)) but a unimolecular (eqn. (2)) reaction of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$. Spectral changes similar to that in Fig. 1(a) were observed under the conditions in Fig. 1(b) (see 'Supplementary material', Fig. S1). The observed first-order rate constants k_{obs} at 478, 415, 361 and 286 nm under the conditions in Fig. 1(b) were 0.0116, 0.0125, 0.0127 and 0.0117 s^{-1}, respectively, and their good agreement with each other supports reaction (2). Only the data at 286 nm were obtained in a twice diluted solution (0.05 mM $Pt^{II}_2Pt^{III}_2$), since the absorbance measured under the same condition (0.1 mM) in Fig. 1(b) was very large (in the range 1–2) so that this calculated k_{obs} value showed a large deviation from the others. Although the absorbance at 478 nm decreases to less than *c.* 1% of the initial absorbance at the final equilibrium state, the band does not completely disappear. Therefore, the reaction can be regarded as a reversible process and the equilibrium is largely shifted to the side of the dimers. The disproportionation constant K_{disp} for reaction (2) is *c.* 1×10^{-2} M and the molar extinction coefficient of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ at 478 nm is *c.* 5×10^4 M^{-1} cm^{-1}, estimated from the calculated values of A_0 and A_∞ in eqn. (3). Considering that the reverse reaction is a second-order reaction and that the first-order plot for the decrease in absorbance at 478 nm is linear for at least 6 half-lives, the contribution of the reverse reaction and other side reactions seems to be negligibly small. Although oxidation of the Pt^{II}_2 dimer to the Pt^{III}_2 dimer by molecular oxygen slowly occurs under air atmosphere, its contribution to the titled reaction can be neglected, for the first-order rate constant for this reaction is smaller than 4.2×10^{-5} s^{-1} under these conditions (the details will be separately reported elsewhere).

The rate of the disproportionation reaction was found to be sensitive to both $[H^+]$ and $[SO_4^{2-}]$. The k_{obs} values, obtained for solutions containing x M H_2SO_4 and $(0.25-x)$ M Na_2SO_4 ($x=0.061$–0.25) at 25 °C, can be expressed by eqn. (4), where $k_1=3.9\times10^{-2}$ s^{-1} and $k_2=5.3\times10^{-4}$ M s^{-1}. On the other hand, under a

$$k_{obs} = k_1 = \frac{k_2}{[H^+]} \tag{4}$$

constant H^+ concentration (0.29 M) and at various sulfate concentrations (0.023–0.044 M) with $I=0.75$ M at 25 °C, the value of k_{obs} increases from 0.016 to 0.040 s^{-1} with decreasing $[SO_4^{2-}]$. However, the details of the interactions have not yet been clarified.

The disproportionation reaction of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ is slow enough to be measured by normal spectroscopic techniques in acidic media, but the reaction completes within a second in neutral aqueous media. The half-life of the reaction at pH = 5 in the presence of 0.25 M Na_2SO_4 can be estimated to be 13 ms (25 °C) by using the obtained k_{obs} from eqn. (4). Figure 2(a) shows a ^1H NMR spectrum of free α-pyrrolidone in D_2O. Figure 2(b) is a spectrum for a solution of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$, in which two different sets of α-pyrrolidonate ligands are observed with the integrated intensity ratio of *c.* 1:1. The two sets can be assigned to the signals of the Pt^{II}_2 and Pt^{III}_2 dimers, as illustrated in Fig. 2(b), from the results described in the following. When an equimolar amount of $K_2S_2O_8$ was added to the $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ solution, one of the two sets in the higher field disappeared and the intensities of the remaining signals almost doubled (Fig. 2(c)). The reaction of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ with $K_2S_2O_8$

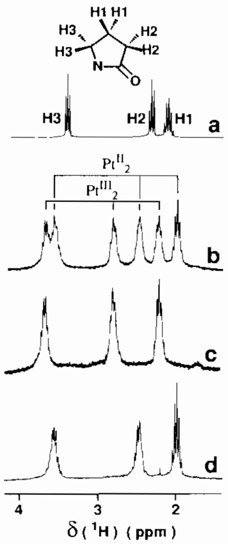


Fig. 2. ^1H NMR spectra at 23 °C (a) Free α-pyrrolidone in D_2O, δ 2.12 (tt, 2H), 2.34 (t, 2H, $J=7.9$ Hz), 3.42 (t, 2H, $J=7.1$ Hz) ppm (b) 2 mM $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2(NO_3)_6 \cdot 2H_2O$ in D_2O, where δ 2.01 (tt, 4H), 2.43–2.58 (m, 4H), 3.47–3.65 (m, 4H) ppm are assigned to the Pt^{II}_2 dimer and δ 2.18–2.33 (m, 4H), 2.75–2.90 (m, 4H), 3.65–3.85 (m, 4H) ppm are assigned to the Pt^{III}_2 dimer. (c) $K_2S_2O_8$ (2 mM) was added to the solution in (b) δ 2.25 (tt, 4H), 2.73–2.93 (m, 4H), 3.57–3.87 (m, 4H) ppm (d) Hydroquinone (2 mM) was added to the solution in (b). δ 2.00 (tt, 4H, $J=7.5$ Hz), 2.40–2.60 (m, 4H), 3.45–3.70 (m, 4H) ppm

produces $[Pt^{III}_2(NH_3)_4(C_4H_6NO)_2LL']^{4+}$ ($L=OH_2$ and $L'=OH^-$, under these conditions), as eqn. (5) shows, and therefore, one of the sets in the lower field is assigned to the Pt^{III}_2 dimer.

$$[Pt^{II}_2(NH_3)_4(C_4H_6NO)_2]^{2+} + S_2O_8^{2-} + L + L' \longrightarrow [Pt^{III}_2(NH_3)_4(C_4H_6NO)_2LL']^{4+} + 2SO_4^{2-} \quad (5)$$

On the contrary, the lower field set disappeared upon addition of an equimolar amount of hydroquinone (Fig. 2(d)), which is ascribed to reaction (6). In this

$$[Pt^{III}_2(NH_3)_4(C_4H_6NO)_2LL']^{4+} + \text{hydroquinone} \longrightarrow [Pt^{II}_2(NH_3)_4(C_4H_6NO)_2]^{2+} + 2H^+ + \text{quinone} + L + L' \quad (6)$$

measurement, the formation of quinone was observed as a singlet at 6.87 ppm but hydroquinone (6.80) ppm was not detected. The total integrated intensity in the α-pyrrolidonate region with respect to that of DSS did not significantly change before and after each redox reaction described above. Furthermore, it does not seem probable that the signals of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ are overlapping with those of the dimers. Therefore, the equilibrium in reaction (2) is largely shifted towards the dimers in neutral aqueous media. A ^1H NMR spectrum of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ in 0.5 M D_2SO_4/D_2O (acquired in air at 25 °C by an hour accumulation), under comparable conditions to those of the UV–Vis studies described above, was similar to Fig. 2(b), but the signal intensity of the Pt^{III}_2 dimer was twice as large as that of the Pt^{II}_2 dimer (Fig. 3). The contribution of the oxidation reaction of the Pt^{II}_2 dimer to the Pt^{III}_2 dimer by molecular oxygen (first-order rate constant is 4.2×10^{-5} s^{-1}, in 0.5 M H_2SO_4 at 25 °C in air) cannot be neglected in NMR measurements, which requires a longer accumulation time compared to UV–Vis measurements. On the contrary, in neutral aqueous media, reduction of the Pt^{III}_2 dimer to the Pt^{II}_2 dimer by water was observed. However, this reaction rate is extremely slow and it takes 4 days to change the abundance ratio of the dimers from 50/50 to 48/52.

Finally, we examined the axial ligand substitution reaction of the Pt^{III}_2 dimer by observing the absorption band at 286 nm, which shows a growth during the disproportionation of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ (Fig. 1(a)). A Pt^{III}_2 dimer stock solution was prepared according to eqn. (5) and was used to prepare solutions of the Pt^{III}_2 dimer with various hydrogen and sulfate ion concentrations. The absorption spectrum of this stock solution was identical to that of a solution of $[Pt^{III}_2(NH_3)_4(C_4H_6NO)_2(NO_3)(OH_2)](NO_3)_3$ (see 'Experimental'). As a result of the experiment, it was found that the absorption spectrum is sensitive to both $[H^+]$ and $[SO_4^{2-}]$ and that the spectral change on addition of either acid or sulfate was so rapid that each spectrum observed corresponds to the equilibrated state of each solution. Dependence of the spectrum on $[H^+]$ could be attributed to the dissociation equilibrium of the axially coordinated aqua ligand of the Pt^{III}_2 dimer. It was confirmed that the addition of either perchlorate or nitrate does not affect the spectrum of the Pt^{III}_2 dimer solution. From the latter observation,

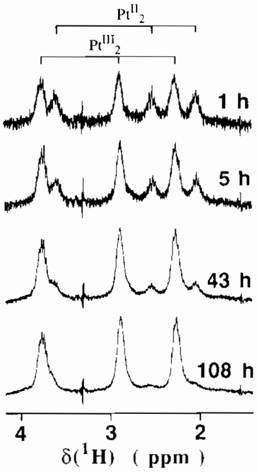


Fig 3 The time course of ^1H NMR spectra $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2(NO_3)_6 \cdot 2H_2O$ (2 mM) was dissolved in 0.5 M D_2SO_4/D_2O at 23 °C in air.

we suggest that the axial nitrate ligand in the complex $[\mathrm{Pt^{III}}_2(NH_3)_4(C_4H_6NO)_2(NO_3)(OH_2)](NO_3)_3$ is rapidly replaced by an aqua ligand when the complex is dissolved in aqueous solutions. Therefore, it seems natural to think that the $\mathrm{Pt^{III}}_2$ dimer takes two aqua ligands in the absence of sulfate anions. The contribution of the hydroxo-coordinated $\mathrm{Pt^{III}}_2$ dimer can be neglected under the relatively high acidic conditions, since the pK_a value has been spectrophotometrically determined to be *c.* 3 (to be published separately elsewhere). Therefore, dependence of the spectrum on $[SO_4^{2-}]$ was investigated in the presence of 0.1 M $HClO_4$ (Fig. 4). The spectrum in Fig. 4(a) was measured for a solution prepared by simple dilution of the $\mathrm{Pt^{III}}_2$ dimer stock solution, which contained 0.1 mM SO_4^{2-} converted from added $S_2O_8^{2-}$ according to eqn. (5). In a separate experiment similarly carried out in the presence of 4.0 M $HClO_4$ and 0.01–0.10 M Na_2SO_4, no significant spectral change was observed with the increase in the amount of Na_2SO_4 added and all the observed spectra were similar to that in Fig. 4(a). Under these conditions, the concentration of SO_4^{2-} was *c.* 2.5% of the added Na_2SO_4 concentration, the remainder being protonated to HSO_4-. Therefore, the drastic spectral change in Fig. 4 can be ascribed to the axial ligand substitution by SO_4^{2-}. Although an isosbestic point is observed at 257 nm in the lower region of the sulfate concentration, it gradually deviates with increasing $[SO_4^{2-}]$, indicating that the shifts of equilibria in eqns. (7) and (8) take place at the same time.

$$H_2O\text{–}\mathrm{Pt^{III}}_2\text{–}OH_2+SO_4^{2-} \overset{K_{S1}}{\rightleftharpoons} H_2O\text{–}\mathrm{Pt^{III}}_2\text{–}OSO_3 \quad (7)$$

$$H_2O\text{–}\mathrm{Pt^{III}}_2\text{–}OSO_3+SO_4^{2-} \overset{K_{S2}}{\rightleftharpoons} O_3SO\text{–}\mathrm{Pt^{III}}_2\text{–}OSO_3 \quad (8)$$

$H_2O\text{–}\mathrm{Pt^{III}}_2\text{–}OH_2$, $H_2O\text{–}\mathrm{Pt^{III}}_2\text{–}OSO_3$ and $O_3SO\text{–}\mathrm{Pt^{III}}_2\text{–}OSO_3$ are abbreviations for the diaqua-, aqua-sulfato- and disulfato-coordinated $\mathrm{Pt^{III}}_2$ dimers, respectively. The Na_2SO_4 concentration was changed in the range of 0–0.10 M, which brought about changes in both $[H^+]$ and $[SO_4^{2-}]$ in the range 0.100–0.0621 M and 0.0505–66.2 mM, respectively. The observed absorbance at 286 nm fits well eqn. (9) (Fig. 5), where $\epsilon_{W,W}$, $\epsilon_{W,S}$ and $\epsilon_{S,S}$ are the molar extinction coefficients of $H_2O\text{–}\mathrm{Pt^{III}}_2\text{–}OH_2$, $H_2O\text{–}\mathrm{Pt^{III}}_2\text{–}OSO_3$ and $O_3SO\text{–}\mathrm{Pt^{III}}_2\text{–}OSO_3$ at 286 nm, respectively, and $[\mathrm{Pt^{III}}_2]_t$ is the total $\mathrm{Pt^{III}}_2$ dimer concentration (0.10 mM).

$$A_{286}=[\mathrm{Pt^{III}}_2]_t \times \frac{\epsilon_{W,W}+\epsilon_{W,S}K_{S1}[SO_4^{2-}]+\epsilon_{S,S}K_{S1}K_{S2}[SO_4^{2-}]^2}{1+K_{S1}[SO_4^{2-}]+K_{S1}K_{S2}[SO_4^{2-}]^2} \quad (9)$$

The obtained parameters are as follows: $K_{S1}=3.4(6)\times 10^2\ M^{-1}$, $K_{S2}=26(6)\ M^{-1}$, $\epsilon_{W,W}=3.03(5)\times 10^3\ M^{-1}\ cm^{-1}$, $\epsilon_{W,S}=9.9(9)\times 10^3\ M^{-1}\ cm^{-1}$ and $\epsilon_{S,S}=1.94(5)\times 10^5\ M^{-1}\ cm^{-1}$. As for the first step in reaction (7), there seems to be two possibilities for the coordination of sulfate, since the two axial coordination sites of $H_2O\text{–}\mathrm{Pt^{III}}_2\text{–}OH_2$ are chemically non-equivalent. It is expected that the coordination of sulfate selectively occurs at either side of the dimer, for an isosbestic point is observed at 257 nm in the lower region of the sulfate concentration. The higher acceptor ability of the $N_2O_2\text{–}\mathrm{Pt^{III}}$ atom compared to that of the $N_4\text{–}\mathrm{Pt^{III}}$ atom has been evidenced in the previous structure analyses of the α-pyrrolidonate-bridged $\mathrm{Pt^{III}}_2$ dimers, such as nitrato-nitrito- [16] and nitrato-chloro-coordinated [17] dimers. Examples can also be found in the structure analyses of several analogous $\mathrm{Pt^{III}}_2$ dimers with different amidate ligands, such as α-pyridonate [11, 18] and 1-methyluracilate [19]. They also support the dinuclear nature of the $\mathrm{Pt^{III}}$ complexes in aqueous media. The difference in the $\mathrm{Pt^{III}}$ electron density will be caused by the difference of the electronegativity between oxygen and nitrogen atoms. In addition, similar spectral behavior has been observed by using either

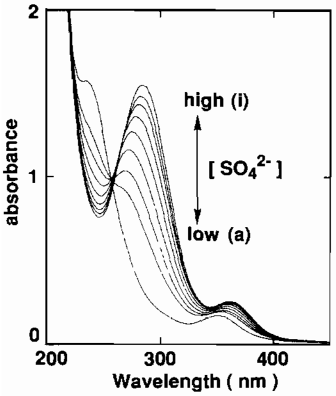


Fig. 4. Absorption spectra of 0.1 mM $\mathrm{Pt^{III}}_2$ dimer with various $[SO_4^{2-}]$ (added as Na_2SO_4) in the presence of 0.1 M $HClO_4$ at 15 °C and $I=0.90$ M ($NaClO_4$). The added Na_2SO_4 concentrations for (a)–(i) are 0.0 (0.314), 0.00581 (0.692), 0.0116 (0.862), 0.0201 (1.035), 0.0334 (1.195), 0.0501 (1.324), 0.0667 (1.423), 0.0800 (1.48) and 0.100 (1.552) M, respectively In each parenthesis, the corresponding absorbance at 286 nm is given.

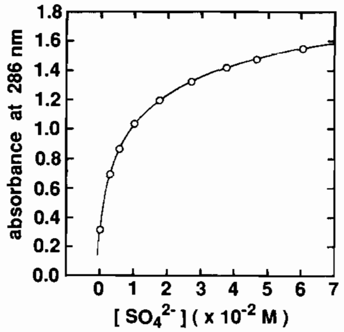


Fig 5. Absorbance at 286 nm in Fig. 4 as a function of $[SO_4^{2-}]$. The solid line is a calculated line according to eqn. (9).

chloride [17, 20] or nitrite [17] anions instead of sulfate. Therefore, the first step in eqn. (7) would also occur selectively at the N_2O_2–Pt^{III} atom. We conclude from these results that the absorption band at 286 nm in Fig. 1(a) corresponds to a mixture of aqua-sulfato- and disulfato-coordinated Pt^{III}_2 dimers. The results also indicate that the empty axial coordination site of the Pt^{III}_2 dimer formed on cleavage of $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ must be rapidly filled with either a sulfate of aqua ligand.

In conclusion, the present study reveals that the mixed-valent tetranuclear complex cation $[Pt^{II}Pt^{III}(NH_3)_4(C_4H_6NO)_2]_2^{6+}$ is not stable in aqueous media and a solution prepared by dissolving the tetramer can be regarded as a 1:1 mixture of the homovalent dimers $[Pt^{II}_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ and $[Pt^{III}_2(NH_3)_4(C_4H_6NO)_2LL']^{4+}$. The present study also shows that the nature of the axial ligands L and L′ in the Pt^{III}_2 dimer depends on the concentrations of coexisting anions.

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