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Crystal Structure and ^{13}C NMR of α-Pyrrolidonato-bridged $[Pt(III)_2(NH_3)_4(C_4H_6NO)_2(NO_2)(NO_3)](NO_3)_2\cdot H_2O$ and Conversion of the Binuclear into Tetranuclear Complex on Electrochemical Redox Reaction

Takeya ABE, Hiroshi MORIYAMA,† and Kazuko MATSUMOTO*
Department of Chemistry, School of Science and Engineering,
Waseda University, Okubo, Shinjuku-ku, Tokyo 169
†National Chemical Laboratory for Industry, 1-1, Higashi, Tsukuba, Ibaraki 305

α-Pyrrolidonato-bridged binuclear Pt(III) complex $[Pt_2(NH_3)_4(C_4H_6NO)_2(NO_2)(NO_3)](NO_3)_2\cdot H_2O$ has been synthesized and the crystal structure, ^{13}C NMR, and cyclic voltammetry are reported. It has been revealed that both binuclear Pt(III) complex and tetranuclear Pt(III) complex are produced from the oxidation of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ depending on the oxidizing agent used.

Amidate-bridged mixed-valent tetranuclear platinum complexes have attracted interest of many chemists, owing to the novel structures and redox properties. The authors have isolated tetranuclear complexes with a basically identical structure but different oxidation states by using α-pyrrolidone as bridging ligand, i.e. $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{n+}$ (n = 5, 6, and 8), whose platinum average oxidation state is 2.25, 2.5, and 3.0, respectively.$^{1-4)}$ The authors have already reported tetranuclear Pt(III) cation $[Pt(III)_4(NH_3)_8(C_4H_6NO)_4]^{8+}$ obtained from the oxidation of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ by $S_2O_8^{2-}$ in strongly acidic medium.$^{4)}$ In the present study oxidation of the same cation $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ was carried out with conc. HNO_3 and it was found that binuclear $[Pt(III)_2(NH_3)_4(C_4H_6NO)_2(NO_2)(NO_3)]^{2+}$ cation $\underset{\sim}{1}$ is produced under the present oxidation condition. The crystal structure and the redox properties are investigated and novel dimer-tetramer conversion has been observed during the electrochemical redox reaction. The present study is the first report showing the existence of both binuclear and tetranuclear amidate-bridged platinum complexes for this class of compounds.

The binuclear complex was prepared by suspending 0.1 g of $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O^{1)}$ in 10 ml of 3 mol dm^{-3} HNO_3. After the solution was left at rt for a week, yellow prism crystals appeared (yield 60%). Found: C, 11.23; H, 2.75; N, 16.01%. Anal. Calcd for $[Pt_2(NH_3)_4(C_4H_6NO)_2(NO_2)(NO_3)](NO_3)_2\cdot H_2O$: C, 10.96; H, 2.99; N, 15.98%.

A yellow crystal of approximate dimensions of 0.09 x 0.10 x 0.10 mm^3 was used for X-ray crystallographic study. The crystal data are as follows: FW = 876.57, monoclinic, space group $P2_1/c$, a = 10.019(2), b = 25.196(6), c = 9.714(4) Å, β = 112.39(2), V = 2267.4 Å^3, D_{calcd} = 2.57, D_{measd} = 2.61 g cm^{-3} and Z = 4. The X-ray diffraction intensities were collected in the range $3° \leq 2\theta \leq 50°$ on a Rigaku

AFC-5R diffractometer with graphite-monochromated Mo Kα radiation. A total of 2851 independent reflections with $|Fo| \geq 4\sigma(|Fo|)$, corrected for Lorentz, polarization, and absorption effects, were used for calculation. The structure was solved by the standard heavy atom method. All non-hydrogen atoms were refined anisotropically by the block-diagonal least-squares method. The final R and R_w ($w = 1/\sigma^2(F)$) factors were 0.0446 and 0.0467, respectively.

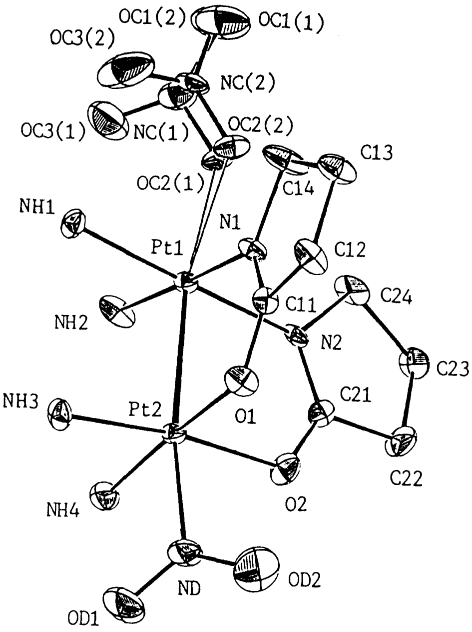

Fig. 1. Structure of $[Pt(III)_2(NH_3)_4(C_4H_6NO)_2(NO_2)(NO_3)]^{2+}$.

The structure of the complex is shown in Fig. 1. Each platinum atom is coordinated by two nitrogen atoms of ammine ligands and either two exocyclic amide oxygens or two deprotonated amide nitrogens. The two α-pyrrolidonate ligands bridge the two platinum atoms in a head-to-head manner. Nitrite anion coordinates axially to the platinum atom coordinated by two amide oxygens, while nitrate anion coordinates to the platinum atom coordinated by two amide nitrogen atoms. The complex structure is analogous to the previously reported α-pyridonate-bridged dimeric platinum complex, $[Pt(III)_2(en)_2(C_5H_4NO)_2(NO_2)(NO_3)](NO_3)_2\cdot 0.5H_2O$[5] in the sence that both complexes are head-to-head isomer and nitrite is coordinated to the N_2O_2-coordinated Pt, while nitrate is coordinated to N_4 coordinated Pt. This selective coordination of nitrite to N_2O_2-coordinated platinum atom seems to result from the less sterically hindered coordination site, compared with N_4-coordinate platinum atom. Coordination of the nitrite with a bent structure to the N_4 coordinated platinum atom would be more hindered, since the platinum coordination site is less open for incoming nitrite due to the projection of the amide ring toward

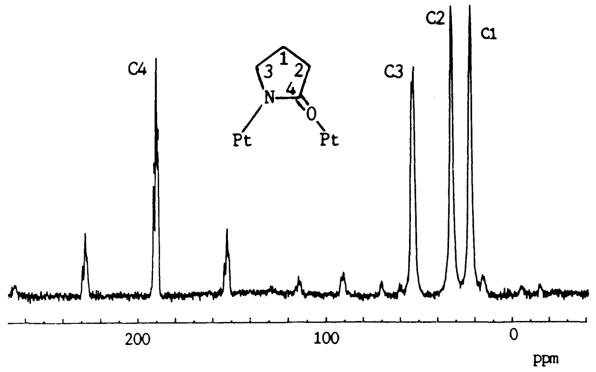

Fig. 2. CP-MAS ^{13}C NMR of $[Pt_2(NH_3)_4(C_4H_6NO)_2(NO_3)](NO_3)_2\cdot H_2O$. The small bands at both sides of a large peak are side bands.

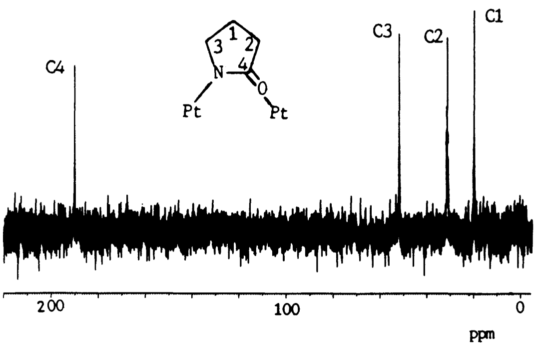

Fig. 3. ^{13}C NMR of $[Pt_2(NH_3)_4(C_4H_6NO)_2(NO_2)(NO_3)](NO_3)_2\cdot H_2O$ in 0.05 mol dm^{-3} H_2SO_4.

the coordination site. Nitrate anion occupies two disordered orientations with equal probabilities as shown in Fig. 1. Selected coordination distances are listed in Table 1. The complex is diamagnetic and stable in air. Figures 2 and 3 are ^{13}C NMR spectra of the complex in solid and 3.6 mol dm^{-3} D_2SO_4 solution, respectively. The two figures show that the solid structure is retained in solution and no isomerization occurs between head-to-head and head-to-tail isomers. Head-to-head to head-to-tail isomerization is reported for similar α-pyrrolidonate-bridged Pt(II) dimer, $[Pt(II)_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ **2**, whose isomerization equilibrium is clearly observed in ^{13}C NMR spectrum as closely lying two peaks for each carbon atom. These two carbon peaks suggest the existence of the two isomers.[6] In the present ^{13}C NMR, no such close-lying double lines are observed.

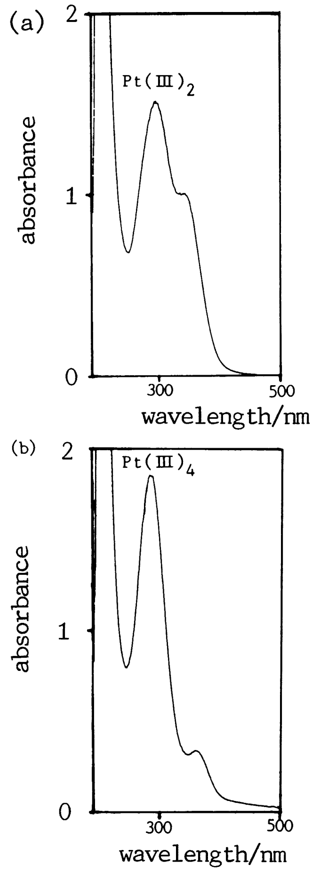

Fig. 4. Ultraviolet spectra of $[Pt_2(NH_3)_4(C_4H_6NO)_2(NO_2)-(NO_3)](NO_3)_2 \cdot H_2O$ in 0.05 mol dm^{-3} H_2SO_4. (a) before electrochemical reduction. (b) after electrochemical reoxidation.

The cyclic voltammogram of the present complex in 0.05 mol dm^{-3} H_2SO_4 shows in the first cycle a pair of irreversible wave at E_{pc} = 0.12 V vs. SCE and E_{pa} = 0.70 V, however, in the second and further repetitive cycles, a new quasi-reversible peak appears with increasing intensity at E_{pc} = 0.48 V and E_{pa} = 0.55 V ($E_p = (E_{pc} + E_{pa})/2$ = 0.52 V) and the original irreversible wave gradually decreases. The former irreversible wave corresponds to the reaction **1** + 2e $\rightleftarrows$ **2** + NO_2^- + NO_3^-. Ultraviolet spectrum after bulk reductive electrolysis of the present complex at -0.2 V in 0.05 mol dm^{-3} H_2SO_4 shows a shoulder at 240 nm, which is identical with the spectrum of previously reported **2**.[6] The latter quasi-reversible wave corresponds to the reaction $[Pt(III)_4(NH_3)_8(C_4H_6NO)_4]^{8+}$ **3** + 4e $\rightleftarrows$ 2 x **2**, since the redox potential is identical with that of formerly reported redox couple of **2** and **3**.[7] UV spectra of the original and reoxidized solution of the once reduced solution in 0.05 mol dm^{-3} H_2SO_4 are shown in Fig. 4. The spectra show reoxidized species is not the original **1**, instead it is tetrameric **3**, which was confirmed by UV spectra (λ_{max}'s for **1** are 294 and 343 nm, while they are 286 and 361 nm for **3**[8] in 0.05 mol dm^{-3} H_2SO_4). Therefore, it turns out that electrochemical reduction of **1** produces **2**, which is in turn oxidized to **3** electrochemically and this irreversible oxidation accounts for the appearances of the two redox couples in the cyclic voltammogram.

The present study reveals for the first time that two oxidized forms , **1** and **3**, exist for $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$, and that the condition under which each of the oxidized forms is produced depends mainly on the oxidizing agent used. **1** is produced on nitric acid oxidation, whereas **3** is produced on persulfate oxidation. Nitrate is reduced in the nitric acid oxidation reaction to nitrite, which easily coordinates to the platinum atom and eventually ruptures the tetrameric structure into dimeric **1**. On the other hand, in the oxidation of the same complex with $S_2O_8{}^{2-}$, tetranuclear Pt(III) complex **3** is produced.4) The latter reaction seems due to the relatively weak coordination ability of sulfate which exists as medium (the reaction is carried out in strongly acidic H_2SO_4 solution) or is produced from $S_2O_8{}^{2-}$ in the reaction.

Table 1. List of distances in Å

	Coordination sphere		
PT1 - PT2	2.644(1)	PT1 - OC2(2)	2.36(2)
PT1 - N1	2.00(1)	PT2 - O1	1.99(1)
PT1 - N2	2.02(1)	PT2 - O2	2.01(1)
PT1 - NH1	2.05(1)	PT2 - NH3	2.05(1)
PT1 - NH2	2.08(1)	PT2 - NH4	2.03(1)
PT1 - OC2(2)	2.36(3)	PT2 - ND	2.10(2)
	Ligand geometry		
N1 - C11	1.30(2)	C23 - C24	1.56(2)
O1 - C11	1.29(2)	C24 - N2	1.49(3)
C11 - C12	1.52(2)	NC(1) - OC1(1)	1.32(4)
C12 - C13	1.54(3)	NC(1) - OC2(1)	1.21(4)
C13 - C14	1.59(3)	NC(1) - OC3(1)	1.17(4)
C14 - N1	1.49(2)	NC(2) - OC1(2)	1.20(4)
N2 - C21	1.28(2)	NC(2) - OC2(2)	1.19(3)
O2 - C21	1.32(2)	NC(2) - OC3(2)	1.24(5)
C21 - C22	1.52(3)	ND - OD1	1.21(2)
C22 - C23	1.55(3)	ND - OD2	1.22(2)
	Anion geometry		
NA - OA1	1.26(2)	NB - OB1	1.27(2)
NA - OA2	1.19(3)	NB - OB2	1.23(2)
NA - OA3	1.15(3)	NB - OB3	1.24(2)

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