Inorganica Chimica Acta, 120 (1986) L1–L3 L1

Synthesis and Electrochemical Properties of Bis[μ-α-pyrrolidonato(1–)-*N,O*] bis[*cis*-diammineplatinum-(II)] (Pt–Pt) Cation

K. MATSUMOTO and N. MATOBA

Department of Chemistry, School of Science and Engineering, Waseda University. Okubo, Shinjuku-ku, Tokyo 160, Japan

(Received May 6, 1986)

Recently several platinum blue related tetranuclear platinum cations with a general formula of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{n+}$ ($n = 5$ [1, 2], 6 [3, 4] and 8 [5]) have been isolated, where C_4H_6NO is deprotonated α-pyrrolidone anion. Titrimetric and photometric studies of $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ indicate that dark brownish red $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ (**1**) is gradually reduced to blue $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$ (**2**) and further to a yellow Pt(II) species (**3**) by water [2]. This reduction reaction is reversible and addition of Ce^{4+} or $Na_2S_2O_8$ to **2** or **3** restores the visible spectrum of **1**. The study also shows that **1** is reversibly oxidized to a yellow Pt(III) species (**4**) by O_2 in a strongly acidic solution. The oxidation product (**4**) has recently been isolated and confirmed to be a tetranuclear cation, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$ [5]. In the present study, a yellow Pt(II) dimer (**3**) has been isolated from the reduction of **1** with OH^-. Although a similar dimeric α-pyridine complex, $[Pt_2(NH_3)_8(C_5H_4NO)_2]^{2+}$ has been reported previously [8], the present synthetic method is simpler and reproducible. The redox behavior of **3** is also investigated by means of cyclic voltammetry.

Experimental

The synthetic procedure of **3** was as follows. 50 mg of $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ [3, 4] was dissolved in 5 ml of water. After 50 mg of $NaPF_6$ was added to the solution, 2,4 M NaOH was added gradually to the solution until the solution turned completely yellow and precipitation occurred. About 50 μl of 2.4 M NaOH was consumed for the reaction. Excess NaOH addition resulted in the decomposition of the complex. The yellow precipitate was cooled with ice-water and then filtered. Perchlorate salt of **3** was similarly obtained by the addition of 50 mg of $LiClO_4$ instead of $NaPF_6$. The complexes were formulated as $[Pt_2(NH_3)_4(C_4H_6NO)_2](PF_6)_2$ and $[Pt_2(NH_3)_4(C_4H_6NO)_2](ClO_4)_2$, based on elemental analyses, IR measurements, electric conductivity measurements and other chemical properties, as described below. *Anal.* Calc. for $[Pt_2(NH_3)_4(C_4H_6NO)_2](PF_6)_2$: C, 10.48; H, 2.64; N, 9.17. Found for hexafluorophosphate salt: C, 10.40; H, 2.88; N, 9.62%. Calc. for $[Pt_2(NH_3)_4(C_4H_6NO)_2](ClO_4)_2$: C, 11.63; H, 2.94; N, 10.18. Found for perchlorate salt: C, 11.92; H, 2.82; N, 9.88%. All the other platinum complexes $[Pt_4(NH_3)_6(C_4H_6NO)_4](PF_6)_3(NO_3)_2 \cdot 5H_2O$ [2], $Pt_4(NH_3)_8(C_4H_6NO)_4(NO_3)_6 \cdot 2H_2O$ [3], $[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_5 \cdot H_2O$ [6] and $[Pt_2(NH_3)_4(C_5H_4NO)_2]_2(NO_3)_4$ [8], used for IR and conductivity measurements were prepared according to the reported methods.

IR spectra were recorded on a Hitachi 260-50 spectrometer. Solution conductivity measurements were performed with a TOA CM-20E conductivity meter. Cyclic voltammetry measurements were carried out with a Fuso 315A potentiostat using a platinum plate working electrode and a platinum wire counter electrode. Coulometry was performed with a Yanaco V10-CM coulometer. Gas chromatographic and GC–MS analyses of the gas produced by the reaction of **1** with OH^- were carried out with Shimadzu GC-9A and Shimadzu GCMS-9P1000, respectively.

Results and Discussion

Figure 1a shows IR spectrum of $[Pt_2(NH_3)_4(C_4H_6NO)_2](PF_6)_2$. For comparison, IR spectrum of tetranuclear $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_3(NO_3)_2 \cdot$

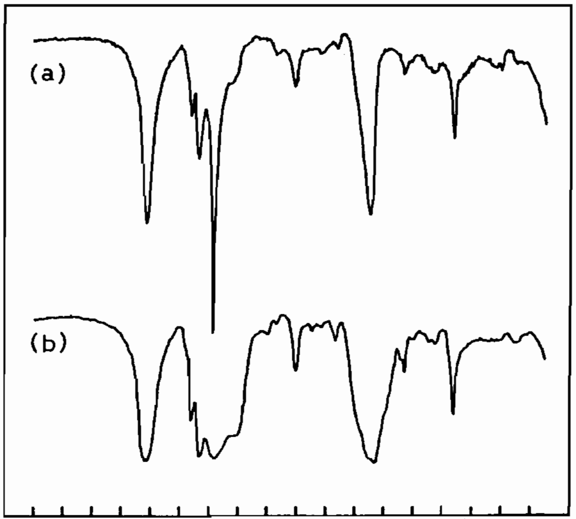

Fig. 1. IR spectra measured as KBr pellets. (a) $[Pt_2(NH_3)_4(C_4H_6NO)_2](PF_6)_2$, (b) $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_3(NO_3)_2 \cdot 5H_2O$.

0020-1693/86/$3.50

$5H_2O$ is shown in Fig. 1b. Both complexes show similar spectra, indicating their structures and coordination modes are basically the same. The broadenings of the bands at ~1400 and ~820 cm^{-1} in $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_3(NO_3)_2 \cdot 5H_2O$ are caused by overlapping NO_3^- bands.

In order to confirm the dimeric nature of **3** in an aqueous solution, electric conductivity measurements were carried out for **3** and other platinum blue related tetrameric and dimeric complexes. The results are shown in Figs. 2 and 3. From Fig. 2 it is observed that, for the cations with a basically similar structure and the same average platinum oxidation state, the slope of the linear line is little affected by the difference of the ligand or counter anions, since α-pyrrolidone complex $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_3(NO_3)_2 \cdot 5H_2O$ and α-pyridone complex $[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_5 \cdot H_2O$ exhibit almost the same slope. Increase of the average platinum oxidation state decreases the slope of the line, as observed for $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_3(NO_3)_2 \cdot 5H_2O$ and $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$, which is expected from the Onsagar's equation [7]. In Fig. 3 the conductivities of $[Pt_2(NH_3)_4(C_4H_6NO)_2](PF_6)_2$ (**3**) and also dimeric Pt(II) α-pyridone compound $[Pt_2(NH_3)_4(C_5H_4NO)_2]_2(NO_3)_4$ are shown. The latter compound is reported to be dimeric in solution, although it is tetrameric in solid state [8]. The close similarity of the lines in Fig. 3 shows that **3** is also dimeric in solution.

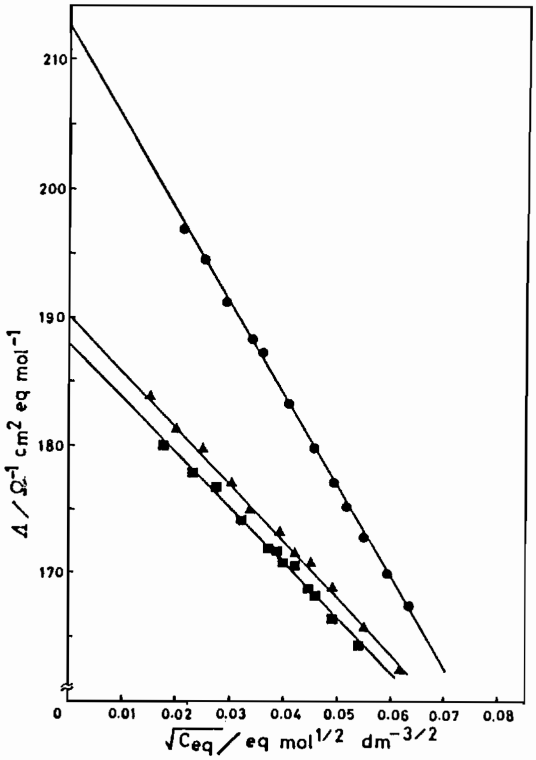

Fig. 2. Solution electric conductivities of $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ (–●–), $[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_5 \cdot H_2O$ (–▲–) and $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_3(NO_3)_2 \cdot 5H_2O$ (–■–) in aqueous solutions.

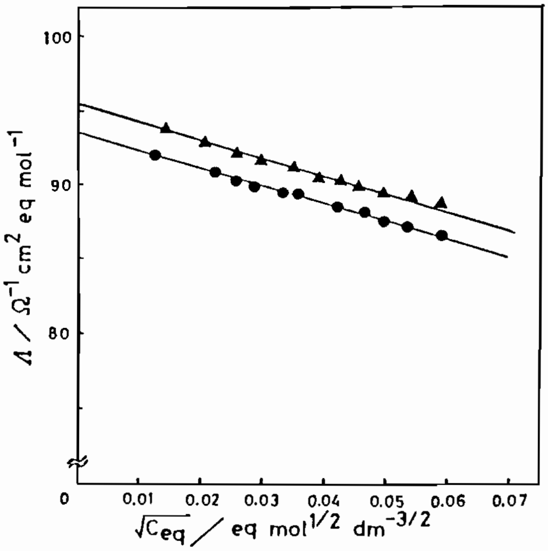

Fig. 3. Solution electric conductivities of $[Pt_2(NH_3)_4(C_5H_4NO)_2]_2(NO_3)_4$ (–▲–) and $[Pt_2(NH_3)_4(C_4H_6NO)_2](PF_6)_2$ (–●–) in aqueous solutions.

An aqueous solution of **3** is gradually oxidized to blue **2** by O_2 on long standing. On addition of either Ce^{4+} or $Na_2S_2O_8$, **3** is rapidly oxidized to **1**, **2** and **4**. These reactions were confirmed by UV–Vis spectra (λ_{max} for **1**, 478 nm ($\epsilon = 3.9 \times 10^4$ cm^{-1} M^{-1}), 415 nm ($\epsilon = 1.5 \times 10^4$ cm^{-1} M^{-1} in 4.5 M H_2SO_4; λ_{max} for **2**, 660 nm ($\epsilon = 3.4 \times 10^2$ cm^{-1} M^{-1}) in H_2O; λ_{max} for **4**, 361 nm ($\epsilon = 1.7 \times 10^3$ cm^{-1} M^{-1})).

Concerning the oxidation product of OH^{-1} as a result of the redox reaction with **1**, the authors carried out gas chromatographic analysis of the gas in the head space of a sealed tube containing an aqueous solution of **1** with pH 8*. Molecular oxygen was detected. The O_2 was confirmed to originate from water by GC–MS analysis of the gas using $H_2{}^{18}O$. Therefore, the reaction is described as follows

$$2[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+} + 2OH^- \rightleftharpoons 4[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+} + O_2 + 2H^+$$

Recently the authors have reported similar oxidation reaction of **4** oxidizing OH^- into O_2 [5]. These

---

*Experimental conditions for the gas chromatographic analysis were those described in ref. 5.

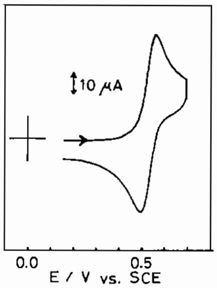

Fig. 4. Cyclic voltammogram of $[Pt_2(NH_3)_4(C_4H_6NO)_2]$-$(PF_6)_2$ (0.6 mM in 4.5 M H_2SO_4, sweep rate 0.1 V s^{-1}).

facts reveal an interesting redox chemistry of the tetranuclear platinum compound that the cation oxidizes OH^- to O_2 in two subsequent oxidation steps.

Cyclic voltammetry of $[Pt_2(NH_3)_4(C_4H_6NO)_2]$-$(PF_6)_2$ (**3**) was carried out in 4.5 M H_2SO_4. The result is shown in Fig. 4. A single redox wave is observed ($E_{pa} = 0.56$, $E_{pc} = 0.49$ and $E_p = (E_{pa} + E_{pc})/2 = 0.53$ V *vs.* SCE) in the region examined, from 0.0 to 1.0 V. In bulk oxidative electrolysis of the solution at 0.8 V, the initially yellow solution turned blue and then gradually to green, dark red and finally to yellow. This color change corresponds to the oxidation of **3**, into **2**, **1** and **4**, which was confirmed by UV–Vis spectra. Cyclic voltammetry conducted after the bulk electrolysis gave result identical to that in Fig. 4 and also that of authentic sample of **4**. Bulk reductive electrolysis at 0.2 V of the oxidized solution restored **3**. Coulometry in the bulk oxidative electrolysis resulted in the net loss of 2.1 electrons per **3**, indicating the redox wave in Fig. 4 as a whole corresponds to the following reaction.

$$2[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+} \overset{-4e}{\rightleftharpoons} [Pt_4(NH_3)_8(C_4H_6NO)_4]^{8+}$$

The peak separation between E_{pc} and E_{pa} could not be decreased less than 0.07 V with any scan rate from 0.001 to 0.5 V s^{-1}. This fact together with the color change in the process of the bulk electrolysis suggests the redox reaction is basically irreversible and consists actually of very closely lying two or more precesses. The appearance of blue color in the bulk oxidative electrolysis signifies that at least the first oxidative step would be one or two electron process

$$[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+} \xrightarrow{-e} [Pt_2(NH_3)_4(C_4H_6NO)_2]^{3+}$$

or

$$[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+} \xrightarrow{-2e} [Pt_2(NH_3)_4(C_4H_6NO)_2]^{4+}$$

The blue **2** would be formed by either one of the following reactions,

$$[Pt_2(NH_3)_4(C_4H_6NO)_2]^{3+} + [Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+} \longrightarrow [Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+} \quad (2)$$

or

$$[Pt_2(NH_3)_4(C_4H_6NO)_2]^{4+} + 3[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+} \longrightarrow 2[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$$

Similar seemingly a single wave but actually two closely neighboring redox waves are reported for head-to-head α-pyridone Pt(III) dimer, $[Pt_2(NH_3)_4(C_5H_4NO)_2(H_2O)(NO_3)]^{3+}$. The redox reaction in this case is

$$\mathrm{Pt(III)–Pt(III)} + e \rightleftharpoons \mathrm{Pt(II)–Pt(III)} + e \rightleftharpoons \mathrm{Pt(II)–Pt(II)}$$

The potential difference of the two steps is only 30 mV [9].

The stability of the complex in solution was monitored with both U–Vis spectrum and cyclic voltammetry. It was found that the redox potential is not affected by pH of the solution (Na_2SO_4 0.1 M) and the complex is stable up to pH 11. However, it is decomposed at pHs higher than 11.

References

1 K. Matsumoto and K. Fuwa, *Chem. Lett.*, 569 (1984).
2 K. Matsumoto, *Chem. Lett.*, 2061 (1984).
3 K. Matsumoto and K. Fuwa, *J. Am. Chem. Soc.*, *104*, 897 (1982).
4 K. Matsumoto, H. Takahashi and K. Fuwa, *Inorg. Chem.*, *22*, 4086 (1983).
5 K. Matsumoto and T. Watanabe, *J. Am. Chem. Soc.*, *108*, 1308 (1986).
6 J. K. Barton, S. A. Best, S. J. Lippard and R. A. Walton, *J. Am. Chem. Soc.*, *100*, 3785 (1978).
7 T. Shedlovsky, *J. Am. Chem. Soc.*, *54*, 1405 (1932).
8 L. S. Hollis and S. J. Lippard, *J. Am. Chem. Soc.*, *105*, 3494 (1983).
9 L. S. Hollis and S. J. Lippard, *Inorg. Chem.*, *22*, 2605 (1983).