Inorganica Chimica Acta, *121* (1986) L29–L31

Synthesis and Chemical Properties of *cis*-Diammineplatinum 3,3-Dimethylglutarimide Blue

K. MATSUMOTO*, K. TAKAHASHI

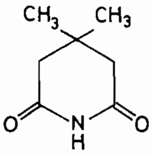
Department of Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjuku-ku, Tokyo 160, Japan

and T. WATANABE

The University of Air, Wakaba, Chiba 260, Japan

(Received July 15, 1986)

A class of tetranuclear platinum complexes generally called 'platinum blues' have attracted the interest of many chemists because of their unusual blue color, novel tetranuclear zigzag chain structure and paramagnetic nature due to the presence of Pt(III). Recent synthetic and spectroscopic studies on *cis*-diammineplatinum α-pyridone blue [1, 2] and *cis*-diammineplatinum α-pyrrolidone-blue and -tan [3, 4] have revealed interesting structures and redox behaviors. In the present study, 3,3-dimethylglutarimide was selected as the lactam ligand and a similar blue complex $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4]^{5+}$ was synthesized in order to see how the chemical properties such as electronic and ESR spectra or redox potential are affected by the substitution of the lactam ligand.



3,3-dimethylglutarimide

Experimental

The complex $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4](NO_3)_5\cdot5H_2O$ was obtained by either one of the following two methods.

(a) *cis*-$Pt(NH_3)_2Cl_2$ (3 mmol) and $AgNO_3$ (6 mmol) were dissolved in 21 ml of H_2O, which was stirred overnight in the dark. After the AgCl precipitate was removed by ultracentrifuge at 2000 rpm for 15 min and filtration, 3 mmol of 3,3-dimethylglutarimide was added to the filtrate. The solution was adjusted to pH 10 by adding 0.5 M NaOH and was left in the dark for 1–2 h at 80 °C. The solution was then cooled to room temperature, adjusted to pH 4 by adding HNO_3 and left standing for a further 2 to 3 h at 80 °C in the dark. At this time the solution turned dark blue. $NaNO_3$ (2.5 g) was added to the blue solution and the solution was kept at 0 °C for 48 h. A dark blue amorphous precipitate of the NO_3^- salt appeared, which was collected by filtration. The PF_6^- salt was similarly obtained by adding $NaPF_6$ instead of $NaNO_3$.

(b) The same procedure was followed until the AgCl-removed filtrate was obtained. To the filtrate 3 mmol of 3,3-dimethylglutarimide was added and the pH was adjusted to 7.2 with 0.5 M NaOH. After the solution was incubated at 80 °C for 2 days in the dark, it turned dark blue. The dark blue precipitate was obtained by adding 2.5 g of $NaNO_3$ to the solution and leaving the solution at 0 °C for 48 h. *Anal.* Calc. for $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4](NO_3)_5\cdot5H_2O$: C, 17.91; H, 3.98; N, 12.68. Found: C, 17.13; H, 3.73; N, 12.07%; Calc. for $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4](PF_6)_4(NO_3)\cdot8H_2O$: C, 14.86; H, 3.57; N, 8.05. Found: C, 14.39; H, 3.41; N, 7.64%.

Platinum(II) dimer complex $[Pt_2(NH_3)_4(C_7H_{10}NO_2)_2](PF_6)_2\cdot5H_2O$ was prepared from $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4]^{5+}$ as follows. Fifty mg of $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4](NO_3)_5\cdot5H_2O$ was dissolved in 2 ml H_2O. To the blue solution 2.4 M NaOH was added until the solution turned yellowish-brown (about 20 μl of 2.4 M NaOH was consumed). On addition of 50 mg of $NaPF_6$ a yellowish-brown precipitate appeared. After precipitation was completed by adding excess acetone and ethanol and by cooling the solution with ice-water, the precipitate was collected by filtration. *Anal.* Calc. for $[Pt_2(NH_3)_4(C_7H_{10}NO_2)_2](PF_6)_2\cdot5H_2O$: C, 14.68; H, 3.09; N, 7.34. Found: C, 14.62; H, 3.03; N, 7.63%.

The average platinum oxidation state was confirmed with potentiometric oxidative titration by using a Ce(IV) solution. The experimental conditions for the titration procedure were those described previously [4].

Cyclic voltammetry was conducted for 1 mM $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4](NO_3)_5\cdot5H_2O$ solution containing 0.5 M Na_2SO_4 on a Nikko Keisoku DPGS-1 potentiostat. The pH of the solution was varied from 0 to 7 by adding 1:1 H_2SO_4. A platinum plate working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE) were used for measurement. Coulometry was performed with a Yanaco V10-CM coulometer.

UV–Vis. spectra were recorded on a Shimadzu UV-260 spectrometer. Infrared measurements of the samples were conducted as KBr pellets on a Hitachi 260-50 infrared spectrophotometer.

ESR spectra measurements were performed on a JEOL FE1X spectrometer with 100 kHz magnetic field modulation at 77 K.

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

Results and Discussion

Oxidative potentiometric titration of $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4](NO_3)_5 \cdot 5H_2O$ exhibited one end point which corresponds to the oxidation of 0.75 e per one platinum atom. No oxidation occurred to 3,3-dimethylglutarimide alone under the same redox titration conditions. Thus the result confirms the average platinum oxidation state of $Pt^{2.25+}$, which would actually be a mixture of Pt(II) and Pt(III) at a 3:1 molar ratio and agrees with the proposed formula.

ESR spectra of a powder and an aqueous solution of $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4](PF_6)_4(NO_3) \cdot 8H_2O$ are shown in Fig. 1. The powder signal (a) is characterized by a broad axial signal, whereas that of an aqueous solution (b) is accompanied by hyperfine splitting due to platinum atoms (I = 1/2, 33.7% natural abundance). Although theoretical simulation for the hyperfine splitting in Fig. 1b is currently impossible, its resemblance to the ESR spectrum of *cis*-diammineplatinum α-pyrrolidone tan tetramer [6] suggests that the present compound would also be a tetramer. Similarly broad and ill-resolved hyperfine lines are reported for platinum 1-carboxycyclohexane-2-carboxamide blue and so far no satisfactory explanation is given for it [7]. It seems that the present complex is decomposed in DMSO, since no ESR signal was observed in DMSO.

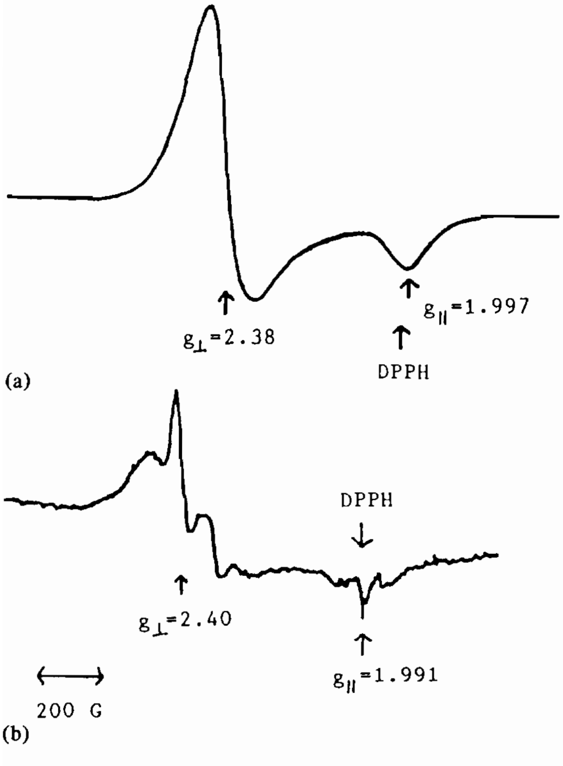


Fig. 1. X-band ESR spectra of $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4](PF_6)_4(NO_3) \cdot 8H_2O$: (a) powder, (b) aqueous solution.

An aqueous solution of $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4](NO_3)_5 \cdot H_2O$ exhibits broad absorption maxima at $\lambda = 570$ nm ($\epsilon = 4.1 \times 10^3$ cm^{-1} mol^{-1} dm^3) and $\lambda = 670$ nm ($\epsilon = 5.2 \times 10^3$ cm^{-1} mol^{-1} dm^3). The solution is stable at least for 4 h, which is in contrast to the gradual reduction of α-pyrrolidone-blue or -tan cation on dissolution in water [5].

Cyclic voltammetry of $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4](NO_3)_5 \cdot 5H_2O$ is shown in Fig. 2. A pair of irreversible redox waves is observed ($E_{pa} = 0.24$, $E_{pc} = 0.08$ and $E_p = (E_{pa} + E_{pc})/2 = 0.16$ V *vs.* SCE) in the region examined, from −0.2 to 1.0 V. In bulk oxidative electrolysis of the solution at 0.8 V, the initially blue solution turned yellow at the end of the electrolysis and coulometry showed that the oxidation reaction corresponds to 2.9 electrons per $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4]^{5+}$. Cyclic voltammetry of the oxidized solution just after electrolysis showed a voltammogram basically similar to that in Fig. 2. However, the intensities of the redox peaks gradually decreased with time and after 30 min no redox peaks were observed. Therefore, it seems that the oxidized product is unstable on long standing in an aqueous solution. On the other hand, when the solution of $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4]^{5+}$ is reduced at −0.2 V, the solution turned brownish-yellow, which was confirmed by coulometry to be 1.0 electron reduction per tetramer. The resulting reduced solution is stable and gives a cyclic voltammogram identical to that in Fig. 2. On bulk oxidative electrolysis of the reduced solution, the solution changes from yellow to blue–green and finally to yellow. Coulometry confirmed that the oxidation corresponds to 4 electron-oxidation per tetramer.

Figure 3 shows the IR spectra of $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4](PF_6)_4(NO_3) \cdot 8H_2O$ and $[Pt_2(NH_3)_4(C_7H_{10}NO_2)_2](PF_6)_2 \cdot 5H_2O$. The similarities between the two spectra indicate that the structures and coordination modes are basically the same. The peak at around 780 cm^{-1} is caused by the existence of NO_3^-. The preparative method for $[Pt_2(NH_3)_4$-

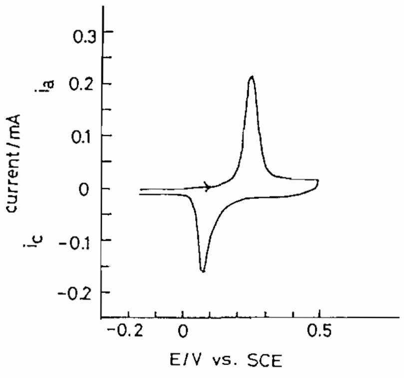


Fig. 2. Cyclic voltammogram of $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4](NO_3)_5 \cdot 5H_2O$ (1 mM in 0.5 M Na_2SO_4, pH 2, sweep rate 0.2 V s^{-1}).

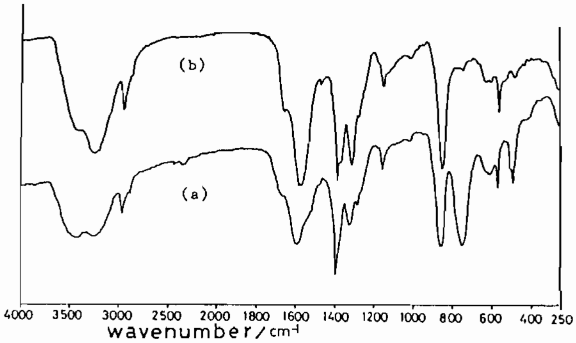


Fig. 3. IR spectra measured as KBr pellets. (a) $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4](PF_6)_4(NO_3)\cdot8H_2O$, (b) $[Pt_2(NH_3)_4(C_7H_{10}NO_2)_2](PF_6)_2\cdot5H_2O$.

$(C_7H_{10}NO_2)_2](PF_6)_2\cdot5H_2O$ follows that of α-pyrrolidone Pt(II) dimer, $[Pt_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ [8], and indicates that the present cation $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4]^{5+}$ is also reduced by OH^-. An aqueous solution of $[Pt_2(NH_3)_4(C_7H_{10}NO_2)_2](PF_6)_2\cdot5H_2O$ exhibits a cyclic voltammogram similar to that in Fig. 2.

From the cyclic voltammetric and coulometric studies together with the IR spectra, it is concluded that the reaction in the first anodic sweep in Fig. 2 would correspond to the following 3-electron oxidation, $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4]^{5+} \xrightarrow{-3e} 4 \times Pt(III)$, and in the cathodic sweep, the reaction $4 \times Pt(III) \xrightarrow{4e} 2[Pt_2(NH_3)_4(C_7H_{10}NO_2)_2]^{2+}$ takes place. Although we expected Pt(III) tetramer $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4]^{8+}$ as an oxidation product by analogy with the similar oxidation reaction of *cis*-diammineplatinum α-pyrrolidone tan [6], no satisfactory elemental analyses were obtained for an electrochemically or chemically oxidized product, which would probably be due to the instability of the oxidized complex as mentioned earlier. The appearance of a blue–green color in the bulk oxidative electrolysis of once reduced solution suggests that the redox peaks actually consist of several redox steps involving the formation of blue $[Pt_4(NH_3)_8(C_7H_{10}NO_2)_4]^{5+}$.

Acknowledgements

The authors thank the Japanese Ministry of Health and Welfare for the financial support.

References

1 J. K. Barton, H. N. Rabinowitz, D. J. Szalda and S. J. Lippard, *J. Am. Chem. Soc., 99,* 2827 (1977).
2 J. K. Barton, D. J. Szalda, H. N. Rabinowitz, J. V. Waszezak and S. J. Lippard, *J. Am. Chem. Soc., 101,* 1434 (1979).
3 K. Matsumoto, H. Takahashi and K. Fuwa, *Inorg. Chem., 22,* 4086 (1983).
4 K. Matsumoto, H. Takahashi and K. Fuwa, *J. Am. Chem. Soc., 106,* 2049 (1984).
5 k. Matsumoto, *Chem. Lett.,* 2061 (1984).
6 K. Matsumoto and T. Watanabe, *J. Am. Chem. Soc., 108,* 1308 (1986).
7 P. Arrizabalaga, P. Castan, M. Geoffrey and J.-P. Laurent, *Inorg. Chem., 24,* 3656 (1985).
8 K. Matsumoto and N. Matoba, *Inorg. Chim. Acta,* in press.