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CRYSTAL STRUCTURE OF cis-DIAMMINEPLATINUM α-PYRROLIDONE VIOLET, $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_2(NO_3)_{2.56}\cdot 5H_2O$

Kazuko MATSUMOTO* and Keiichiro FUWA
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Crystal structure of cis-diammineplatinum α-pyrrolidone violet, $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_2(NO_3)_{2.56}\cdot 5H_2O$ is reported. From the results of X-ray diffraction analysis and potentiometric oxidative titration, it has been found that the compound is nonstoichiometric, being a mixture of 44% of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{4+}$ and 56% of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$ with the average platinum oxidation state of 2.14.

Recently much attention has been paid to a class of compounds called "platinum blues" because of their unusual color, paramagnetic nature and oligomeric structures.[1-4] Several structural analyses have been carried out and it has turned out that the compound consists of amidate-bridged tetrameric chain cation formally containing Pt(II) and Pt(III) atoms. The cations thus far reported are cis-diammineplatinum α-pyridone blue cation,[5] $[Pt_4(NH_3)_8(C_5H_4NO)_4]^{5+}$ (1), cis-diammineplatinum α-pyridone yellow,[6] $[Pt_4(NH_3)_8(C_5H_4NO)_4]^{4+}$ (2), cis-diammineplatinum α-pyrrolidone tan,[7,8] $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ (3), and cis-diammineplatinum α-pyrrolidone green,[9] $[Pt_4(NH_3)_8$

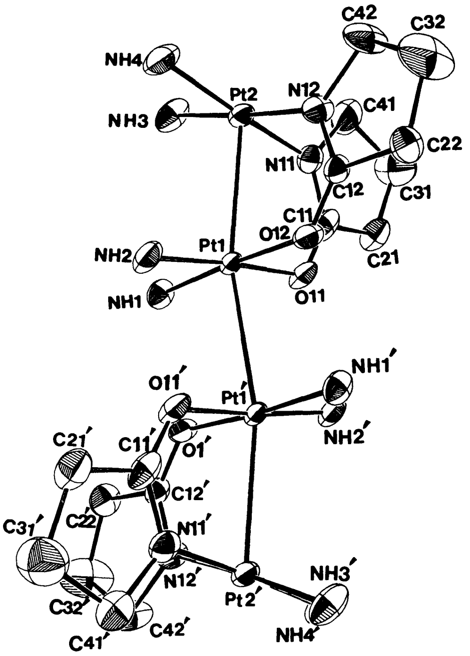

Fig. 1. Structure of $(Pt_4(NH_3)_8(C_4H_6NO)_4]^{4.56}$. The cation is actually a mixture of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{4+}$ and $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$. The thermal ellipsoids are drawn with 50% probability.

Table 1. Geometric Comparison of Tetranuclear Platinum-blue Related Compounds

Compound	Av Pt	Distance/ Å			
	Oxdn State	Pt-Pt	$Pt-NH_3$(av)	Pt-N(av)	Pt-O(av)
cis-Diammineplatinum α-Pyridone Yellow (2)	2.0	2.88a) 3.13b)	2.05	2.05	2.04
cis-Diammineplatinum 1-Methylhydantoin Yellow	2.0	3.131a) 3.204b)	2.04	2.00	2.05
cis-Diammineplatinum α-Pyridone Blue (1)	2.25	2.7745a) 2.8770b)	2.027	2.026	2.019
cis-Diammineplatinum α-pyrrolidone Green (4)	2.37	2.764a) 2.761a) 2.739b) 2.724b) 2.740a) 2.753a)	2.06	2.07	2.03
cis-Diammineplatinum α-Pyrrolidone Tan (3)	2.5	2.70a) 2.71b) 2.71a)	2.13	2.10	2.06
cis-Diammineplatinum α-Pyrrolidone Violet (5)	2.14	2.848a) 2.839a) 2.875b) 2.875b)	2.05	2.00	1.97

a) Distances related to terminal Pt-Pt bonds.

b) Distances related to central Pt-Pt bonds.

$(C_4H_6NO)_4]^{5.48+}$ (4), which is a nonstoichiometric mixture of pentavalent cation, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$ and 3. In this paper, we report another nonstoichiometric compound, cis-diammineplatinum α-pyrrolidone violet (5), and discuss the structural features in relation to the platinum oxidation state.

The compound 5 was obtained following the same procedure as for 3,7) except that, in the final stage, 0.37 g of $NaPF_6$ was added instead of $NaNO_3$. After the solution was left standing at 5 °C overnight, blue-violet plate crystals appeared.

The crystal structure was solved by standard heavy atom method. The compound is triclinic with the space group $P\bar{1}$. The cell parameters are as follows; a= 13.530(8), b=19.242(9), c=10.222(3) Å, α=96.56(9), β=93.82(9), γ=74.64(8)°, Z=2. The X-ray reflections were collected up to 2θ=55° on a Philips PW1100 diffractometer with graphite monochromated Mo Kα radiation. The measurement was carried out on a crystal sealed in a glass capillary in order to avoid crystal deterioration after long irradiation. A total of 8377 reflections, corrected for Lorentz and polarization effects and also for absorption, were used for refinement. All the atoms except hydrogen atoms have been located and refined anisotropically to the final R factor of 0.090 ($R=\Sigma||Fo| - |Fc||/\Sigma|Fo|$).

The structure of the cation is shown in Fig. 1. Each platinum atom is coordinated by two ammine ligands and either two exocyclic amide oxygens or two deprotonated amide nitrogens. A unit cell contains two crystallographically independent tetrameric cations. The cation has an inversion center at the midpoint of the central Pt-Pt bond and the basic structure is similar to those of **3** and **4**. However, the Pt-Pt distances in **5** are, as shown in Table 1, significantly longer than those found in **3** and **4**, which indicates that the average platinum oxidation state of **5** is lower than those of **3** and **4**. As reported previously, a Pt-Pt distance is closely related to the average platinum oxidation state and, from the correlation curve obtained from previously reported tetrameric compounds,[9] the average oxidation state of **5** is 2.10 (obtained from the terminal Pt-Pt distances) and 2.25 (from the central Pt-Pt distances).

In order to determine the average platinum oxidation state, potentiometric oxidative titration with Ce(IV) was carried out. The details of the method were described previously.[8] The titrations were carried out both in 0.29 M and 0.93 M HNO_3 solutions and both indicate that the average platinum oxidation state is 2.14. Considering the fact that **4** is a nonstoichiometric mixture of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$ and $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$,[9] the present results probably mean that **5** is a mixture of yellow $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{4+}$ and blue $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$. Based on the average platinum oxidation state of 2.14, **5** is considered as consisting of 44% of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{4+}$ and 56% of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$. From the X-ray structural analysis, it has been found that two PF_6^- anions and one tetranuclear cation are located with the weight of unity and four nitrate anions are distributed with the statistical weight of less than unity. From these results, the chemical formula of **5** is $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_2(NO_3)_{2.56}\cdot 5H_2O$. The analytical results are as follows; Found: C, 10.79; H, 3.32; N, 11.70; Pt, 43.4%. Calcd: C, 10.72; H, 3.27; N, 11.38; Pt, 43.55%.

In Table 1, selected structural parameters of tetrameric platinum compounds are compared. It seems that terminal and central Pt-Pt distances are dependent not only on the platinum oxidation state but also on the amide ligand. Although for α-pyridone compounds **1** and **2**, the central Pt-Pt distances are always appreciably longer than the terminal ones (the difference is more than 0.1 Å), the difference is always remarkably small (less than 0.04 Å) for α-pyrrolidone compounds in any platinum oxidation state. Other coordination distances around platinum atoms are also summarized in Table 1. Although slight differences are observed in the coordination distances, they are not significant chemically in view of the relatively large standard deviations (≈0.03 Å). The present work has demonstrated the existence of a nonstoichiometric platinum-blue related compound with the average platinum oxidation state of as low as 2.14.

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