cis-Diammineplatinum α-Pyrrolidone Tan, a Structural Analogue of Platinum Blues

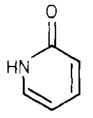
Kazuko Matsumoto* and Keiichiro Fuwa

Department of Chemistry, Faculty of Science
University of Tokyo, Hongo
Bunkyo-ku, Tokyo 113, Japan

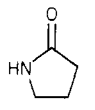
Received August 4, 1981

Platinum blues are a class of compounds that are formed through the reaction of platinum(II) with amide ligands and have attracted much interest because of their unusual color.[1] Recently, interest in these complexes was sparked by the discovery of antitumor activity and low associated nephrotoxicity of platinum pyrimidine blues.[2] Although many studies suggest their paramagnetic, mixed-valent, oligomeric nature,[2-4] their structures have long been unknown because no crystalline platinum blues were obtained. Recently Lippard et al. succeeded in synthesizing crystalline *cis*-diammineplatinum α-pyridone blue (**1**), $[Pt_4(NH_3)_8(C_5H_4ON)_4](NO_3)_5 \cdot H_2O$, and revealed its tetranuclear amidate-bridged chain structure.[5,6] This structure determination was certainly a large step toward the understanding of the chemistry of platinum blues; however, many synthetic and spectroscopic studies on the platinum pyrimidine blues show that the solution chemistry of platinum blues are very complicated, and there are expected to be more than one oligomeric platinum species existing in solution. For instance, many investigators have experienced that the color and the elemental composition of the compound differs from batch to batch.[2,3] We have thus undertaken a detailed study in order to clarify other species possibly coexisting in the solution.

In this paper, we report the synthesis and the crystal structure of *cis*-diammineplatinum α-pyrrolidone tan (**2**), $[Pt_4(NH_3)_8(C_4H_6ON)_4](NO_3)_6 \cdot 3H_2O$, obtained from the reaction of the *cis*-diammineplatinum(II) hydrolysis product with α-pyrrolidone. Platinum tan has been reported by some workers to appear[3,7,8] when synthesizing platinum blues, but no detailed study has been undertaken. The striking result of the present study is that the basic structure of **2** (Figure 1) is similar to that of *cis*-diammineplatinum α-pyridone blue (**1**), that is, head-to-head, amidate-bridged tetranuclear compound; however, platinum oxidation state in the present compound (**2**) is 2.5, whereas that of *cis*-diammineplatinum α-pyridone blue (**1**) is 2.25.



α-pyridone



α-pyrrolidone

cis-Diammineplatinum α-pyrrolidone tan was obtained by adding 7 mL of 0.15 M solution of *cis*-diammineplatinum(II) hydrolysis product[10] to 1 mmol of α-pyrrolidone. After adjusting the pH of the solution approximately to 7 with 0.1 N NaOH, the solution was incubated in the dark at 80 °C for 4 h until a dark red color appeared in the solution. After cooling the solution to room temperature, a few drops of nitric acid and 0.75 g of sodium nitrate were added to the solution. The solution was then allowed to stand for 24 h at −5 °C and dark red irregular plate crystals appeared. The elemental analyses are as follows. Anal. Calcd for $[Pt_4(NH_3)_8(C_4H_6ON)_4](NO_3)_6 \cdot 3H_2O$: C, 11.44; H, 3.24; N, 15.02; Pt, 46.47. Found: C, 11.24; H, 3.09; N, 14.70; Pt, 46.1. Sometimes a dark green or dark blue color appeared in the solution after the reaction at 80 °C for 4 h, but they all turned dark red when the solution was allowed to stand at −5 °C, and the product obtained was always the same in either case. The water solution of compound **2** is unstable at room temperature and is converted to a blue solution after several hours.

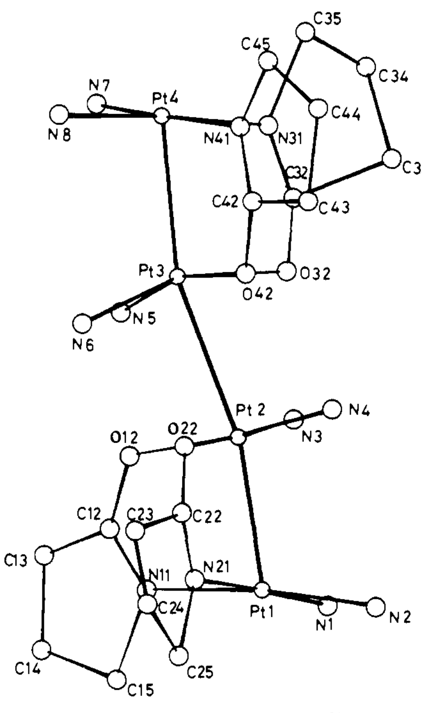


Figure 1. Structure of $[Pt_4(NH_3)_8(C_4H_6ON)_4]^{6+}$. All the atoms are independent crystallographically, but the cation conforms approximately to $\bar{1}$ symmetry; the center of symmetry is located at the center of the Pt2–Pt3 bond axis.

The crystal of compound **2** is monoclinic, space group $P2_1/c$ with the following cell constants: a = 14.960 (81), b = 16.254 (7), c = 19.164 (96) Å; β = 115.10 (37)° for Z = 4. The structure was solved by the heavy-atom method using 3435 independent reflections collected with Mo Kα radiation up to 2θ = 55° on a Philips four-circle diffractometer. Refinement with anisotropic temperature factors for platinum and isotropic factors for all the other atoms except hydrogen atoms has converged at a current value of 0.14 for the discrepancy index $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.[9]

The structure of the $[Pt_4(NH_3)_8(C_4H_6ON)_4]^{6+}$ cation is depicted in Figure 1. It has a geometry basically identical with that of α-pyridone blue (**1**);[5,6] however, the most important difference is that the average platinum oxidation state for the present compound (**2**) is 2.50, whereas that of compound **1** is 2.25. More striking, while the present structural analysis proceeded, is that Lippard et al. reported another greenish yellow tetranuclear platinum α-pyridone compound **3**, $[Pt_4(NH_3)_8(C_5H_4ON)_4](NO_3)_4$.[10] The structure of **3** is also identical with that of compounds **1** and **2**, but the platinum oxidation state is 2.0 for compound **3**. Therefore, the subtle differences of the colors so far reported for

---

[1] (a) Hofmann, K. A.; Bugge, G. *Chem. Ber.* **1908**, *41*, 312. (b) Gillard, R. D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2835.

[2] (a) Davidson, J. P.; Faber, P. J.; Fischer, R. G., Jr.; Mansy, S.; Peresie, H. J.; Rosenberg, B.; Van Camp, L. *Cancer Chemother. Rep.* **1975**, *59*, 287. (b) Rosenberg, B. *Ibid.* **1975**, *59*, 589. (c) Speer, R. J.; Ridgway, H.; Hall, L. M.; Stewart, D. P.; Howe, K. E.; Lieberman, D. Z.; Newman, A. D.; Hill, J. M. *Ibid.* **1975**, *59*, 629. (d) Hill, J. M.; Loeb, E.; MacLellan, A.; Hill, N. O.; Khan, A.; King, J. J. *Ibid.* **1975**, *59*, 647.

[3] Lippert, B. *J. Clin. Hematol. Oncol.* **1977**, *7*, 26.

[4] (a) Burness, J. H.; Bandurski, M. J.; Passman, L. J.; Rosenburg, B. *J. Clin. Hematol. Oncol.* **1977**, *7*, 508. (b) Flynn, C. M., Jr.; Viswanathan, T. S.; Martin, R. B. *J. Inorg. Nucl. Chem.* **1977**, *39*, 437.

[5] Barton, J. K.; Robinowitz, H. N.; Szalda, D. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 2827.

[6] Barton, J. K.; Szalda, D. J.; Rabinowitz, H. N.; Waszezak, J. V.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 1434.

[7] Laurent, M. P.; Tewksbury, J. C.; Krogh-Jespersen, M.-B; Patterson, H. *Inorg. Chem.* **1980**, *19*, 1656.

[8] Barton, J. K.; Caravana, C.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 7269.

[9] All the nitrate anions and water molecules were identified, but there seems to be some disorder about their distribution in the crystal lattice, and preliminary Weissenberg photographs exhibited diffuse reflections.

[10] Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 1230.

Table I. Geometric Comparison of Three Tetranuclear Platinum Blue Related Compounds

compd	color	av Pt ox. state	Pt-Pt, Å	Pt-Pt-Pt, deg	ref
1	blue	2.25	2.774 2.877	164.60	5, 6
2	dark red	2.50	2.702 2.709	170.44 168.75	*a*
3	greenish yellow	2.0	2.88 3.13		10

[a] This work.

a class of compounds called under the generic name "platinum blues" seem to be due to the differences of the average platinum oxidation state, and the present study revealed the characteristic nature of these compounds—they are oligomeric amidate-bridged platinum compounds, whose platinum oxidation state changes to various degrees without basic structural change. This nature resembles that of one-dimensional platinum chain compounds. Platinum blues might be a suitable class of compounds for the study of Pt–Pt interactions of the chain compounds in the solution phase.

The differences of the platinum oxidation states in the three compounds are also reflected in the Pt–Pt distances, as shown in Table I. The Pt–Pt distance of the three tetranuclear complexes increases as the Pt oxidation state decreases, a correlation similar to that observed for one-dimensional platinum complexes.[11,12] Other examples of bridged platinum(II) or platinum(III) dimers and their Pt–Pt distances are as follows: 3.229 and 3.11 Å in *cis*-diammineplatinum(II) pyrophosphate dimer,[13] 2.97 Å in *cis*-diammineplatinum(II) 1-methylthyminato head-to-tail dimer,[14] 2.91 Å in *cis*-diammineplatinum(II) 1-methylthyminato head-to-head dimer,[15] 2.90 Å in *cis*-diammineplatinum(II) α-pyridone head-to-tail dimer,[10] and 2.466 Å in sulfate-bridged Pt(III)–Pt(III) dimer.[16] These values for bridged Pt–Pt complexes are somewhat shorter than those found in the nonbridged one-dimensional compounds with corresponding oxidation states as pointed out earlier.[5] Moreover, we should also note the recently reported very interesting example of bridged platinum compound, *cis*-nitrodiammineplatinum 1-methylcytosinato head-to-tail dimer,[17] whose platinum oxidation state is also 2.5 and the Pt–Pt distance is 2.584 Å. Each of the platinum atoms in this compound is definitely coordinated by a nitro group (Pt–N = 2.12 and 2.13 Å) in the axial position and accordingly can be considered as six-coordinated. This situation is markedly different from that of the present compound; the platinum atoms in the present compound are very loosely coordinated by nitrate groups at both ends of the Pt chain and the Pt–O (nitrate anion) distances are larger than 3 Å. The Pt–Pt distances (2.702 and 2.709 Å) are significantly larger than that of 1-methylcytosinato dimer. Therefore, Pt–Pt distances seem to be related to how the platinum atoms are coordinated in the axial position as well as to the platinum oxidation state. In order to discuss fully these relations and the factors which determine the Pt–Pt distance, further confirmation of the platinum oxidation state with other methods such as oxidation–reduction titration or susceptibility measurement are desired.[18] Such experiments are now under way. The Pt–Pt chain is not straight in any platinum blue related compounds. The Pt–Pt–Pt angles are summarized in Table I, and the angles in the present compound (**2**), 170.4 and 168.8°, are somewhat larger than those found in platinum α-pyridone blue. To answer the question whether this zigzag chain angles have any correlation with the platinum oxidation state, we have to await the detailed report on compound **3**. The platinum coordination planes are canted to each other. The angles between the planes are 18.68° between Pt1 and Pt2 and 21.22° between Pt3 and Pt4, while the coordination planes for Pt2 and Pt3 are almost parallel; the angle between them is 1.01°. This canting feature is quite similar to that of α-pyridone blue and is the result of the fact that N···O bite distances of α-pyrrolidone ligand (av 2.40 Å) is shorter than Pt–Pt bond length (2.70 Å). Other details of the structure and solution properties will be published later.

Acknowledgment. This work was supported by a grant for a development of anticancer medicines (No. 23665) from the Japanese Ministry of Health and Welfare.

Supplementary Material Available: Atomic positional and thermal parameters for compound **2** (2 pages). Ordering information is given on any current masthead page.

---

(11) Williams, J. M. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 651.

(12) Reis, A. H., Jr.; Peterson, S. W. *Inorg. Chem.* **1976**, *15*, 3186.

(13) Stanko, J. A.; Cleare, M. J. In "Platinum Coordination Complexes in Chemotherapy"; Connors, T. A., Roberts, J. J., Ed.; Springer-Verlag: New York, 1974; pp 24–26.

(14) Lock, C. J. L.; Peresie, H. J.; Rosenberg, B.; Turner, G. *J. Am. Chem. Soc.* **1978**, *100*, 3371.

(15) Lippert, B.; Neugebauer, D.; Schubert, U. *Inorg. Chim. Acta* **1980**, *46* (B1), L11.

(16) Maraveiskaya, G. S.; Kukina, G. A.; Orlova, V. S.; Evstafeva, O. N.; Porai-Koshits, M. A. *Dokl. Akad. Nauk. SSSR* **1976**, *226*, 596.

(17) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 1111.

(18) Although we considered the possibility that the present complex may contain the pentahydrodioxonium cation as seen in the platinum pyrimidine monomer or dimer complexes (see ref 17 and 19), we cannot definitely say whether such an oxonium cation exists in the present compound, since, as mentioned in ref 9, there seems to be some disorder in the crystal lattice. If the compound contains such an oxonium cation, the platinum oxidation state must be changed to a lower value, and in that case, the relation between the Pt–Pt distance and the platinum oxidation state of the present compound would be nearer to that of platinum 1-methylcytosinato dimer. The formula $(H_5O_2)[Pt_4(NH_4)_8(C_4H_6ON)_4](NO_3)_6{\cdot}H_2O$, whose average platinum oxidation state is 2.25, also gives almost identical calculated elemental concentrations (C, 11.44; H, 3.31; N, 15.01; Pt, 46.44%) with the proposed formula, but as we could not find any definite oxonium cation in the final difference map, we have chosen the proposed formula.

(19) Faggiani, R.; Lippert, B.; Lock, C. J. L. *Inorg. Chem.* **1980**, *19*, 295.

Photochemistry of Surface-Confined Mononuclear and Trinuclear Ruthenium Carbonyl Complexes. Direct Evidence for the Ability To Isolate Photogenerated Intermediates from Each Other on High Surface Area Silica

David K. Liu and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received October 23, 1981

Photoactivation of homogeneous organometallic catalysts by light-induced extrusion of 2-electron donor ligands or metal–metal bond cleavage has been demonstrated.[1-5] A problem that has

---

(1) (a) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979. (b) Graff, J. L.; Sanner, R. D.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 273. (c) Mitchener, J. C.; Wrighton, M. S. *Ibid.* **1981**, *103*, 975. (d) Wrighton, M. S.; Graff, J. L.; Reichel, C. L.; Sanner, R. D. *Ann. N. Y. Acad. Sci.* **1980**, *333*, 188. (e) Austin, R. G.; Paonessa, R. S.; Giordano, P. J.; Wrighton, M. S. *Adv. Chem. Ser.* **1978**, *No. 168*, 189.

(2) King, A. D., Jr.; King, R. B.; Sailers, E. L., III. *J. Am. Chem. Soc.* **1981**, *103*, 1867.

(3) Chase, D. B.; Weigert, F. J. *J. Am. Chem. Soc.* **1981**, *103*, 977.

(4) Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: New York, 1970.

(5) (a) Platbrood, G.; Wilputte-Steinert, L. *J. Organomet. Chem.* **1974**, *70*, 393, 407; **1975**, *85*, 199. *Tetrahedron Lett.* **1974**, 2507. (b) Nasielski, J.; Kirsch, P.; Wilputte-Steinert, L. *J. Organomet. Chem.* **1971**, *27*, C13. (c) Krausz, P.; Carnier, F.; DuBois, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 437. (d) Agapiou, A.; McNelis, E. *J. Chem. Soc., Chem. Commun.* **1975**, *187*. *J. Organomet. Chem.* **1975**, *99*, C47.