state. The importance of this reduction step has been understated in consideration of models for the photosynthetic water oxidation system. To illustrate these points Scheme I shows how a manganese–semiquinone complex might function as a catalyst in a water oxidation system that uses a plastoquinone (PQ) as an electron acceptor. The scheme begins with a dimeric bis(semiquinone)manganese(II) complex which, in the initial step, forms an adduct by addition of two water molecules. Deprotonation of the aquo ligands is accompanied by transfer of two electrons from the metal to the quinone ligands, which affects oxidation of the metal *without oxidation of the complex unit.* Charge stored on the quinone ligands can later be returned to the metals in a photolytic ligand-to-metal charge-transfer step that leads to O_2 formation and reduction of the metal ions. The two-electron-transfer process and intense charge-transfer band in the visible spectrum of $\mathrm{Mn(3,5\text{-}DBCat)_2(py)_2}$ demonstrate the feasibility of this step. Oxygen displacement leaves the Mn(II)–catecholate dimer $\mathrm{[Mn(Cat)_2]_2^{4-}}$. This complex is similar to the product obtained by treating Mn(II) with 3,5-di-*tert*-butylcatechol, procedure 2 in the Experimental Section, which upon oxidation gives $\mathrm{Mn_4(3,5\text{-}DBSQ)_8}$.

There is no evidence that the sequence of reactions outlined in this scheme is related specifically to steps in photosynthetic water oxidation. But the scheme shows how ligands that support reversible two-electron transfer with manganese can affect reversible intramolecular charge separation with the metal ions during the oxygen production process. It further suggests an interesting line of research for the manganese–quinone complexes.

Acknowledgment. Research carried out at the University of Colorado was supported by the NIH under Grant GM-23386. Work at the University of Illinois was funded by NIH Grant HL-13652.

Registry No. $\mathrm{Mn_4(O_2C_6H_2(\mathit{t}\text{-}Bu)_2)_8}$, 78519-35-4; $\mathrm{Mn(O_2C_6H_4(\mathit{t}\text{-}Bu)_2)_2(NC_5H_5)_2\cdot 2NC_5H_5}$, 78470-59-4; $\mathrm{Mn^{II}(3,5\text{-}DBSQ)_2(py)_2}$, 78470-58-3; $\mathrm{Mn_2(CO)_{10}}$, 10170-69-1; H_2O, 7732-18-5; 3,5-di-*tert*-butyl-1,2-benzoquinone, 3383-21-9; 3,5-di-*tert*-butylcatechol, 1020-31-1.

Supplementary Material Available: Listing of structure factor amplitudes for the $\mathrm{Mn_4(3,5\text{-}DBSQ)_8}$ and $\mathrm{Mn(3,5\text{-}DBCat)_2(py)_2}$ structure determinations (17 pages). Ordering information is given on any current masthead page.

Crystal Structure and Magnetic Susceptibility of a Nonstoichiometric Tetranuclear Platinum Compound, *cis*-Diammineplatinum α-Pyrrolidone Green, $\mathrm{[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_{5.48}\cdot 3H_2O}$

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Abstract: From the reaction of the *cis*-dichlorodiammineplatinum hydrolysis product with α-pyrrolidone, crystals of *cis*-diammineplatinum α-pyrrolidone green (PPG) were obtained. Single-crystal X-ray diffraction analysis shows the compound consists of a tetranuclear chain cation, whose adjacent platinum atoms are bridged by α-pyrrolidone ligands. Each platinum atom is cis coordinated by two ammine ligands and either two exocyclic oxygen atoms or two deprotonated ring nitrogen atoms. The structure of the cation is basically identical with those of recently reported *cis*-diammineplatinum α-pyridone yellow (PPY), $\mathrm{[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_4}$, blue (PPB), $\mathrm{[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_5\cdot H_2O}$, and *cis*-diammineplatinum α-pyrrolidone tan (PPT), $\mathrm{[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O}$. The Pt–Pt distances of PPG, 2.764 (8), 2.739 (8), 2.740 (8), 2.761 (8), 2.724 (8), and 2.753 (9) Å, are intermediate between those of PPB (2.7745 and 2.8770 Å) and PPT (2.702, 2.710, and 2.706 Å), which implies the average platinum oxidation state of PPG may be between those of PPB (2.25) and PPT (2.5). The magnetic susceptibility of PPG at 4.2–293 K obeys the Curie–Weiss law and the effective magnetic moment per tetranuclear platinum unit is 1.30 μ_B, which is far less than the value expected for the presence of one unpaired electron (1.73 μ_B). The low magnetic moment can be reasonably explained by assuming that PPG is a mixture of a PPB-corresponding paramagnetic five-charged cation and a PPT-corresponding diamagnetic six-charged cation. From the value of the measured magnetic moment, existence ratios of both cations were calculated as 52% for $\mathrm{[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}}$ and 48% for $\mathrm{[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}}$, and the average platinum oxidation state is 2.37. As a result, PPG is formulated as a nonstoichiometric compound, $\mathrm{[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_{5.48}\cdot 3H_2O}$.

Recently, a series of platinum compounds called "platinum blues" have attracted the interest of chemists because of their unusual dark blue color and high antitumor activities.[1–3] Efforts have been made to characterize them chemically[4] and spectroscopically,[5,6] however, with only a little definite conclusion that they are paramagnetic and oligomeric.

A recent breakthrough for the study of this class of compounds is the single-crystal X-ray diffraction study of *cis*-diammineplatinum α-pyridone blue (PPB), $\mathrm{[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_5\cdot H_2O}$.[7,8] The compound consists of a tetranuclear chain

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(1) Hofmann, K. A.; Bugge, G. *Chem. Ber.* **1908**, *41*, 312–334.

(2) Brown, D. B.; Burbank, R. D.; Robin, M. B. *J. Am. Chem. Soc.* **1969**, *91*, 2895–2902.

(3) Davidson, P. J.; Faber, P. J.; Fischer, R. G., Jr.; Mansy, S.; Peresie, H. J.; Rosenberg, B.; Van Camp, L. *Cancer Chemother. Rep.* **1975**, *59*, 287–300.

(4) Flynn, C. M., Jr.; Viswanathan, T. S.; Martin, R. B. *J. Inorg. Nucl. Chem.* **1977**, *39*, 437–439.

(5) Lippert, B. J. *Clin. Hematol. Oncol.* **1977**, *7*, 26–50.

(6) Macfarlane, R. D.; Torgensen, D. F. *Science* **1976**, *191*, 920–925.

(7) Barton, J. K.; Rabinowitz, H. N.; Szalda, D. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 2827–2829.

(8) Barton, J. K.; Szalda, D. J.; Rabinowitz, H. N.; Waszczak, J. V.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 1434–1441.

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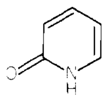
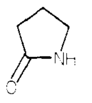
cation, whose adjacent platinum atoms are bridged by exocylic oxygen atoms and deprotonated nitrogen atoms of α-pyridone (**1**).



α-pyridone, 1



α-pyrrolidone, 2

The average oxidation state of the platinum atoms is 2.25; that is, the tetranuclear chain cation formally consists of three Pt(II) atoms and one Pt(III) atom.

We have recently reported a dark red compound, *cis*-diammineplatinum α-pyrrolidone tan (PPT), formulated as $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$, whose cation is structurally similar to that of PPB; however, the average oxidation state of the platinum atoms is 2.5.[9,10] Furthermore, Hollis et al. reported *cis*-diammineplatinum α-pyridone yellow (PPY), $[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_4$, whose structure is also basically similar to those of PPB and PPT, but the average platinum oxidation state is 2.0.[11] These facts reveal the characteristic nature of this class of compounds: that the platinum oxidation state can be varied without basic structural change.

In this paper, the crystal structure and the magnetic susceptibility of the greenish compound, *cis*-diammineplatinum α-pyrrolidone green (PPG), are reported. The compound is nonstoichiometric, being a mixture of PPB corresponding pentavalent cation and hexavalent cation of PPT.

Experimental Section

Preparation of PPG. The compound was prepared as follows: 0.3 g of *cis*-$(NH_3)_2PtCl_2$ and 0.34 g of $AgNO_3$ were stirred overnight in 3.5 mL of H_2O in the dark. After the AgCl precipitate was filtered, 1 mmol of α-pyrrolidone was added to the filtrate, and the solution was adjusted to pH 4.2 with 0.1 N NaOH. The solution was heated at 80 °C for 1 h, while it gradually turned to dark blue-green. After the solution was cooled to room temperature, 0.1 mL of HNO_3 and 0.75 g of $NaNO_3$ were added, and the solution was kept at -5 °C. After 2 days, dark green plate crystals appeared. Anal. Calcd for $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_{5.48} \cdot 3H_2O$: C, 11.67; H, 3.31; N, 14.87; Pt 48.6. Found: C, 11.41; H, 3.31: N 14.72; Pt 48.8. The synthetic procedure described above is almost the same as that for PPT.[9] However, the reaction period is reduced to 1 h, so that air oxidation of platinum would not proceed completely to PPT. It seems that high acidity of the solution accelerates the air oxidation, giving dark red PPT. Therefore, in the present preparation, only 0.1 mL of HNO_3 is added in the final step, instead of 0.6 mL in the PPT preparation.[9]

Collection of the X-ray Data. Crystals of PPG show greenish luster when viewed along the *c* axis with reflecting light. However, it is dark red like PPT when observed along the *c* axis with transmitting light or observed from other directions with either reflecting or transmitting light. The crystal used for collecting the reflection data was a plate of approximate dimensions 0.25 mm in the *b* axis direction, 0.5 mm in the *a* axis, and 0.1 mm in the *c* axis. The crystal was very brittle, and any procedure for shaping was impossible. Preliminary Weissenberg photographs showed the crystal is triclinic. Unit cell parameters were determined from a least-squares fit of 20 reflections in the range $20° < 2\theta < 35°$ measured on a Philips PW1100 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Crystal data and other information related to the data collection are summarized in Table I. The density of the crystal was measured by flotation in a bromoform-chloroform mixture. Intensities were measured with an ω–2θ scan and corrected for Lorentz-polarization effects and absorption. Absorption corrections were applied by using the numerical integration method.[12]

Solution of the Structure. The structure was solved by the heavy-atom method. The coordinates of the platinum atoms were found from three-dimensional Patterson synthesis, and a series of block-diagonal least-squares refinements, first isotropically and later with anisotropic temperature factors, were carried out. The three-dimensional electron density difference synthesis based on the refined coordinates and temperature factors revealed all the non-hydrogen atoms. Although the arrangement of the cations nearly conforms to the centrosymmetric space group $P\bar{1}$, anions and water molecules lie rather in the space group $P1$. Therefore, two independent formula units are contained in a unit cell. Further refinement with anisotropic temperature factors for platinum atoms and isotropic ones for all the other atoms using block-diagonal least-squares resulted in the final discrepancy index of $R_1 = 0.118$ and $R_2 = 0.108$, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and R_2 $[\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2}$. The weight of each reflection was determined as $w_i = 1/\sigma^2(F_o)$. Atomic scattering factors were taken from ref 13, and the anomalous dispersion corrections were based on ref 14.

Table I. Crystal Data and Experimental Conditions for the X-ray Intensity Measurement of *cis*-Diammineplatinum α-Pyrrolidone Green

compound	$[Pt_4(NH_3)_8(C_4H_6ON)_4](NO_3)_{5.48} \cdot 3H_2O$
crystal data	triclinic, space group $P1$
a, Å	12.962 (7)
b, Å	17.931 (10)
c, Å	9.778 (7)
α, deg	99.84 (12)
β, deg	82.45 (9)
γ, deg	108.61 (5)
V, Å^3	2114.8
M_r	1627.3
Z	2
ρ(obsd)	2.64
ρ(calcd)	2.55 g cm^{-3}
μ	139.8 cm^{-1} (for Mo Kα)
scan mode	ω–2θ
scan width	$\omega = 1.2 + 0.3(\tan\theta)$
scan rate	2.0°/min in 2θ
2θ limits	$3.0° < 2\theta < 55°$
transmission factors	0.08–0.18
background measurements	stationary crystal, stationary counter; measurement time = (scan time)/$[2(I_{bck}/I_{int})^{1/2}]$, where I_{bck} is average value of cps preliminary measured at both scan ends and I_{int} is the cps value of the peak
standard	three reflections measured every 2 h showed random, statistical fluctuations
no. of reflections collected	3800
no. of reflections used for calculation	3373 unique reflections for which $|F_o| > 3\sigma|F_o|$

The final nonhydrogen atomic positional parameters are listed in Table II. The final thermal parameters and observed and calculated structure factors are available as Tables S1 and S2, respectively.

Magnetic Susceptibility Measurement. A PAR Model 150A vibrating-sample magnetometer was used to measure the magnetic susceptibility. Powder sample was placed in a container on the tip of the vibrating rod. A total of 29 data points were obtained over a temperature range of 4.2–293 K. The temperature was measured with a copper-constantan thermocouple. The data were corrected for underlying diamagnetism with tabulated values of Pascal constants.[15] The temperature-independent paramagnetism of the compound was obtained from the intercept of the plot of the diamagnetism-corrected susceptibility vs. $1/(T - \theta)$. The value was determined to be 30×10^{-6} cm^3 mol^{-1}.

Results and Discussion

Description of the Structure. The structure of the cation and the atomic numbering scheme are depicted in Figure 1. The cation consists of four platinum atoms linked in a chain with bridging pyrrolidone ligands. Each platinum atom is cis coordinated by two ammine ligands and either two exocyclic oxygen atoms or two deprotonated ring nitrogen atoms of α-pyrrolidone ligands. The central Pt–Pt bonding (Pt2–Pt3) is achieved by partial metal–metal bonding and probably also by hydrogen bonding between ammine hydrogen atoms and exocyclic oxygen atoms of α-pyrrolidone ligands coordinated to adjacent platinum

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(9) Matsumoto, K.; Fuwa, K. *J. Am. Chem. Soc.* **1982**, *104*, 897–898.

(10) Matsumoto, K.; Takahashi, H.; Fuwa, K., *Inorg. Chem.* **1983**, *22*, 4086–4090.

(11) Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 1230–1232.

(12) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180–182.

(13) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, **1974**; Vol. IV, p 92.

(14) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17–23.

(15) Figgis, B. N.; Lewis, J. In "Modern Coordination Chemistry"; Lewis, J., Wilkins, R. G., Eds.; Interscience: New York, 1960; p 440.

Table II. Final Atomic Coordinates with Their Estimated Standard Deviations in Parentheses

	x	*y*	*z*		*x*	*y*	*z*
Pt1[a]	−2911 (3)	2069 (3)	4793 (6)	C64	249 (6)	−88 (8)	−612 (9)
Pt2	−992 (3)	2544 (2)	3121 (5)	O71	−94 (7)	−374 (5)	−158 (7)
Pt3	906 (3)	2655 (2)	1450 (5)	N71	−268 (8)	−418 (8)	−29 (9)
Pt4	2879 (4)	3122 (3)	−68 (7)	C71	−176 (9)	−423 (7)	−119 (10)
Pt5	2902 (4)	−1967 (3)	−4676 (7)	C72	−159 (8)	−508 (8)	−40 (9)
Pt6	976 (3)	−2449 (2)	−3026 (6)	C73	−263 (9)	−544 (9)	32 (10)
Pt7	−907 (3)	−2612 (2)	−1339 (5)	C74	−328 (9)	−488 (8)	43 (9)
Pt8	−2908 (4)	−3024 (3)	164 (8)	O81	−156 (5)	−307 (5)	−308 (7)
NH1	−381 (3)	266 (8)	391 (2)	N81	−336 (9)	−360 (8)	−191 (6)
NH2	−254 (4)	278 (9)	661 (5)	C81	−266 (8)	−327 (7)	−288 (13)
NH3	−147 (6)	318 (7)	195 (3)	C82	−341 (9)	−369 (7)	−413 (8)
NH4	−23 (5)	359 (7)	418 (3)	C83	−445 (8)	−408 (8)	−376 (9)
NH5	92 (4)	162 (6)	166 (2)	C84	−447 (7)	−389 (6)	−224 (7)
NH6	12 (5)	212 (6)	−22 (3)	N1	−139 (9)	−102 (6)	189 (6)
NH7	311 (3)	201 (6)	−51 (5)	OO1	−216 (7)	−132 (5)	130 (5)
NH8	238 (4)	270 (3)	−198 (5)	OO2	−67 (9)	−38 (5)	162 (7)
NH9	378 (7)	−256 (7)	−403 (2)	OO3	−137 (8)	−35 (7)	219 (5)
NH10	250 (2)	−284 (5)	−655 (3)	N2	309 (6)	194 (5)	408 (6)
NH11	146 (5)	−319 (5)	−191 (5)	OO4	379 (6)	183 (4)	306 (5)
NH12	6 (5)	−344 (6)	−436 (3)	OO5	355 (6)	197 (5)	524 (4)
NH13	−94 (2)	−153 (7)	−191 (6)	OO6	212 (5)	203 (3)	441 (4)
NH14	−22 (5)	−214 (7)	48 (5)	N3	−369 (10)	235 (9)	9 (8)
NH15	−342 (3)	−207 (8)	−2 (7)	OO7	−403 (7)	260 (5)	127 (4)
NH16	−243 (3)	−312 (5)	209 (5)	OO8	−273 (4)	241 (4)	−35 (4)
O11	−170 (7)	151 (7)	171 (9)	OO9	−420 (3)	223 (2)	−103 (2)
N11	−322 (8)	110 (5)	299 (4)	N4	838 (8)	506 (9)	510 (8)
C11	−257 (6)	96 (9)	176 (9)	OO10	821 (9)	555 (9)	604 (8)
C12	−337 (6)	52 (6)	83 (8)	OO11	860 (9)	452 (6)	555 (7)
C13	−428 (8)	−10 (7)	167 (7)	OO12	810 (4)	450 (6)	407 (8)
C14	−424 (6)	52 (8)	308 (9)	N5	26 (7)	707 (5)	270 (7)
O21	−37 (7)	186 (6)	427 (5)	OO13	−78 (8)	689 (8)	275 (9)
N21	−205 (7)	145 (6)	545 (10)	OO14	37 (6)	698 (9)	138 (9)
C21	−103 (4)	135 (5)	499 (7)	OO15	21 (9)	647 (7)	313 (7)
C22	−65 (7)	95 (8)	577 (7)	N6	482 (9)	346 (6)	616 (8)
C23	−164 (6)	56 (8)	670 (7)	OO16	473 (6)	354 (5)	742 (9)
C24	−255 (6)	77 (9)	613 (8)	OO17	546 (10)	394 (8)	555 (9)
O31	82 (6)	370 (6)	97 (6)	OO18	388 (7)	308 (9)	600 (7)
N31	254 (9)	417 (7)	5 (7)	N7	−300 (8)	−156 (9)	−376 (10)
C31	166 (6)	433 (6)	54 (6)	OO19	−341 (8)	−147 (7)	−260 (10)
C32	157 (9)	509 (8)	38 (9)	OO20	−373 (5)	−148 (5)	−444 (6)
C33	260 (5)	520 (6)	−60 (9)	OO21	−220 (4)	−162 (4)	−444 (4)
C34	323 (8)	467 (8)	−74 (9)	N8	361 (5)	−210 (3)	7 (3)
O41	171 (7)	325 (6)	308 (7)	OO22	382 (4)	−236 (4)	−119 (5)
N41	342 (8)	364 (10)	182 (7)	OO23	277 (6)	−230 (6)	59 (7)
C41	278 (8)	326 (8)	297 (10)	OO24	399 (5)	−208 (4)	127 (5)
C42	335 (9)	352 (9)	411 (10)	N9	177 (5)	−461 (4)	−465 (5)
C43	456 (9)	385 (8)	351 (9)	OO25	178 (5)	−483 (4)	−603 (7)
C44	454 (10)	378 (10)	193 (8)	OO26	143 (8)	−434 (8)	−558 (10)
O51	167 (8)	−145 (6)	−189 (9)	OO27	207 (5)	−435 (4)	−346 (6)
N51	329 (8)	−118 (9)	−306 (8)	N10	−18 (4)	332 (3)	−212 (4)
C51	264 (9)	−109 (8)	−189 (9)	OO28	83 (5)	355 (3)	−222 (9)
C52	324 (8)	−35 (8)	−114 (7)	OO29	−12 (3)	370 (2)	−90 (4)
C53	433 (7)	−13 (5)	−195 (10)	OO30	−40 (5)	389 (3)	−248 (5)
C54	434 (7)	−50 (9)	−336 (9)	OW1	529 (2)	715 (1)	343 (3)
O61	55 (6)	−180 (4)	−424 (10)	OW2	651 (3)	611 (2)	270 (2)
N61	205 (8)	−149 (9)	−557 (6)	OW3	855 (2)	697 (2)	82 (3)
C61	112 (6)	−137 (9)	−501 (9)	OW4	−397 (3)	422 (1)	−301 (3)
C62	68 (7)	−96 (7)	−578 (8)	OW5	−543 (4)	−280 (4)	314 (5)
C63	172 (9)	−74 (9)	−676 (8)	OW6	−558 (5)	−466 (5)	131 (4)

[a] Coordinates for Pt atoms are multiplied by 10^4 and coordinates for the other atoms are multiplied by 10^3.

atoms. The interatomic distances and bond angles within the cations and nitrate anions are listed in Tables III and IV, respectively. The structure of the cation is basically identical with those of PPB, PPT, and PPY. The Pt–Pt bond distances, which are closely related to the average platinum oxidation state in the tetranuclear platinum chain compound[10] as well as in one-dimensional platinum complexes,[16] are, as Table III shows, intermediate between those of PPB (2.7745 and 2.8770 Å) and PPT (2.702, 2.710, and 2.706 Å). Considering the fact that as the average platinum oxidation state is increased from 2.0 (PPY) to 2.25 (PPB) and 2.5 (PPT), the Pt–Pt distance is decreased from 2.88 to 2.7745 and 2.702 Å, respectively, the Pt–Pt bond length of PPG may suggest that the compound consists of platinum atoms with an intermediate oxidation state between 2.25 and 2.5. Although the compound contains 5.48 nitrate anions per cation as concluded later in the discussion of the magnetic susceptibility measurement, only five nitrate anions have been found in the X-ray diffraction analysis. There still remained some small electron peaks (less than 3% of those of platinum atoms) in the final difference map, and it is concluded that some sort of disorder exists in the crystal lattice. We also considered the possibility that the missing half of the nitrate anion occupies several sites in the crystal lattice with a statistical weight of less than 0.5. However, no electron peak suitable for accommodating a nitrate anion or any other conceivable anions was found. As a result, we cannot

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(16) Reis, A. H., Jr.; Peterson, S. W. *Inorg. Chem.* **1976**, *15*, 3186–3187.

Table III. Interatomic Distances (Å) within the Cations and Nitrate Anions with Their Estimated Standard Deviations in Parentheses

Coordination Spheres			
Pt1-Pt2	2.764 (8)	Pt5-Pt6	2.761 (8)
Pt2-Pt3	2.739 (8)	Pt6-Pt7	2.724 (8)
Pt3-Pt4	2.740 (8)	Pt7-Pt8	2.753 (9)
Pt1-NH1	2.14 (10)	Pt5-NH9	2.01 (11)
Pt1-NH2	2.02 (7)	Pt5-NH10	2.20 (5)
Pt1-N11	2.23 (6)	Pt5-N51	1.93 (10)
Pt1-N21	2.02 (12)	Pt5-N61	1.96 (14)
Pt2-NH3	2.02 (10)	Pt6-NH11	2.13 (9)
Pt2-NH4	2.00 (8)	Pt6-NH12	2.13 (6)
Pt2-O11	2.14 (9)	Pt6-O51	1.96 (9)
Pt2-O21	2.17 (10)	Pt6-O61	2.03 (9)
Pt3-NH5	1.91 (11)	Pt7-NH13	2.12 (12)
Pt3-NH6	1.98 (4)	Pt7-NH14	2.02 (5)
Pt3-O31	2.04 (10)	Pt7-O71	1.99 (9)
Pt3-O41	1.98 (7)	Pt7-O81	1.94 (7)
Pt4-NH7	2.07 (11)	Pt8-NH15	2.06 (14)
Pt4-NH8	2.00 (5)	Pt8-NH16	2.11 (6)
Pt4-N31	2.05 (13)	Pt8-N71	2.14 (15)
Pt4-N41	2.02 (7)	Pt8-N81	2.17 (7)
Pt4-OO16	3.21 (9)	Pt8-OO1	2,95 (15)
Pyrrolidone Rings			
O11-C11	1.24 (12)	O51-C51	1.21 (13)
C11-C12	1.41 (9)	C51-C52	1.44 (15)
C12-C13	1.58 (12)	C52-C53	1.49 (8)
C13-C14	1.61 (12)	C53-C54	1.43 (13)
C14-N11	1.40 (9)	C54-N51	1.54 (15)
N11-C11	1.41 (10)	N51-C51	1.35 (10)
O21-C21	1.28 (8)	O61-C61	1.18 (11)
C21-C22	1.36 (14)	C61-C62	1.42 (14)
C22-C23	1.52 (9)	C62-C63	1.53 (10)
C23-C24	1.55 (14)	C63-C64	1.35 (14)
C24-N21	1.43 (15)	C64-N61	1.24 (15)
N21-C21	1.39 (11)	N61-C61	1.32 (12)
O31-C31	1.38 (11)	O71-C71	1.21 (10)
C31-C32	1.44 (16)	C71-C72	1.90 (16)
C32-C33	1.51 (12)	C72-C73	1.44 (11)
C33-C34	1.42 (16)	C73-C74	1.49 (17)
C34-N31	1.32 (14)	C74-N71	1.48 (14)
N31-C31	1.27 (13)	N71-C71	1.41 (11)
O41-C41	1.38 (13)	O81-C81	1.35 (9)
C41-C42	1.35 (10)	C81-C82	1.59 (12)
C42-C43	1.56 (12)	C82-C83	1.35 (11)
C43-C44	1.54 (12)	C83-C84	1.46 (8)
C44-N41	1.42 (14)	C84-N81	1.43 (11)
N41-C41	1.44 (13)	N81-C81	1.31 (12)
Nitrate Anions			
N1-OO1	1.2 (2)	N6-OO16	1.2 (1)
N1-OO2	1.3 (2)	N6-OO17	1.2 (1)
N1-OO3	1.2 (2)	N6-OO18	1.2 (1)
N2-OO4	1.3 (1)	N7-OO19	1.3 (1)
N2-OO5	1.3 (1)	N7-OO20	1.2 (2)
N2-OO6	1.3 (1)	N7-OO21	1.2 (1)
N3-OO7	1.2 (1)	N8-OO22	1.2 (1)
N3-OO8	1.2 (1)	N8-OO23	1.2 (1)
N3-OO9	1.3 (1)	N8-OO24	1.2 (2)
N4-OO10	1.2 (2)	N9-OO25	1.2 (1)
N4-OO11	1.2 (2)	N9-OO26	1.2 (1)
N4-OO12	1.3 (1)	N9-OO27	1.3 (1)
N5-OO13	1.3 (1)	N10-OO28	1.2 (1)
N5-OO14	1.3 (1)	N10-OO29	1.3 (1)
N5-OO15	1.2 (1)	N10-OO30	1.2 (1)

Table IV. Interatomic Bond Angles (deg) within the Cation with Their Estimated Standard Deviations in Parentheses

Coordination Spheres			
Pt1-Pt2-Pt3	166.6 (3)	Pt5-Pt6-Pt7	168.5 (3)
Pt2-Pt3-Pt4	167.2 (3)	Pt6-Pt7-Pt8	170.9 (3)
NH1-Pt1-NH2	102 (3)	NH9-Pt5-NH10	92 (3)
NH1-Pt1-N11	90 (3)	NH9-Pt5-N51	88 (4)
NH1-Pt1-N21	175 (4)	NH9-Pt5-N61	172 (4)
NH2-Pt1-N11	168 (2)	NH10-Pt5-N51	179 (3)
NH2-Pt1-N21	83 (4)	NH10-Pt5-N61	80 (4)
N11-Pt1-N21	85 (3)	N51-Pt5-N61	100 (4)
NH3-Pt2-NH4	86 (3)	NH11-Pt6-NH12	92 (3)
NH3-Pt2-O11	88 (3)	NH11-Pt6-O51	96 (3)
NH3-Pt2-O21	176 (4)	NH11-Pt6-O61	175 (3)
NH4-Pt2-O11	171 (3)	NH12-Pt6-O51	171 (3)
NH4-Pt2-O21	94 (3)	NH12-Pt6-O61	84 (3)
O11-Pt2-O21	91 (3)	O51-Pt6-O61	87 (3)
NH5-Pt3-NH6	85 (3)	NH13-Pt7-NH14	97 (3)
NH5-Pt3-O31	172 (4)	NH13-Pt7-O71	158 (4)
NH5-Pt3-O41	98 (3)	NH13-Pt7-O81	84 (3)
NH6-Pt3-O31	87 (3)	NH14-Pt7-O71	104 (3)
NH6-Pt3-O41	177 (2)	NH14-Pt7-O81	179 (2)
O31-Pt3-O41	90 (3)	O71-Pt7-O81	76 (3)
NH7-Pt4-NH8	76 (3)	NH15-Pt8-NH16	120 (4)
NH7-Pt4-N31	170 (4)	NH15-Pt8-N71	160 (5)
NH7-Pt4-N41	109 (3)	NH15-Pt8-N81	92 (4)
NH8-Pt4-N31	95 (3)	NH16-Pt8-N71	80 (4)
NH8-Pt4-N41	175 (2)	NH16-Pt8-N81	147 (2)
N31-Pt4-N41	81 (4)	N71-Pt8-N81	68 (4)
Pyrrolidone Rings			
Pt1-N11-C11	132 (5)	Pt5-N51-C51	127 (7)
Pt1-N11-C14	115 (4)	Pt5-N51-C54	112 (5)
Pt2-O11-C11	133 (7)	Pt6-O51-C51	127 (8)
C11-N11-C14	113 (5)	C51-N51-C54	119 (8)
O11-C11-N11	110 (8)	O51-C51-N51	119 (8)
O11-C11-C12	136 (8)	O51-C51-C52	132 (9)
N11-C11-C12	102 (6)	N51-C51-C52	104 (8)
C11-C12-C13	107 (7)	C51-C52-C53	104 (8)
C12-C13-C14	94 (7)	C52-C53-C54	115 (7)
C13-C14-N11	106 (6)	C53-C54-N51	93 (7)
Pt1-N21-C21	132 (7)	Pt5-N61-C61	124 (8)
Pt1-N21-C24	123 (8)	Pt5-N61-C64	121 (8)
Pt2-O21-C21	120 (7)	Pt6-O61-C61	128 (8)
C21-N21-C24	101 (8)	C61-N61-C64	101 (9)
O21-C21-N21	117 (8)	O61-C61-N61	120 (9)
O21-C21-C22	121 (7)	O61-C61-C62	121 (9)
N21-C21-C22	117 (8)	N61-C61-C62	115 (9)
C21-C22-C23	105 (8)	C61-C62-C63	93 (8)
C22-C23-C24	101 (8)	C62-C63-C64	105 (8)
C23-C24-N21	108 (7)	C63-C64-N61	108 (9)
Pt4-N31-C31	128 (8)	Pt8-N71-C71	116 (8)
Pt4-N31-C34	114 (8)	Pt8-N71-C74	127 (8)
Pt3-O31-C31	128 (7)	Pt7-O71-C71	119 (8)
C31-N31-C34	117 (8)	C71-N71-C74	117 (9)
O31-C31-N31	116 (8)	O71-C71-N71	134 (9)
O31-C31-C32	126 (9)	O71-C71-C72	117 (9)
N31-C31-C32	118 (9)	N71-C71-C72	94 (8)
C31-C32-C33	88 (8)	C71-C72-C73	106 (8)
C32-C33-C34	121 (9)	C72-C73-C74	107 (9)
C33-C34-N31	96 (8)	C73-C74-N71	112 (9)
Pt4-N41-C41	114 (7)	Pt8-N81-C81	112 (7)
Pt4-N41-C44	115 (7)	Pt8-N81-C84	122 (5)
Pt3-O41-C41	114 (6)	Pt7-O81-C81	110 (5)
C41-N41-C44	110 (10)	C81-N81-C84	116 (8)
O41-C41-N41	113 (9)	O81-C81-N81	133 (11)
O41-C41-C42	118 (9)	O81-C81-C82	121 (8)
N41-C41-C42	109 (8)	N81-C81-C82	96 (7)
C41-C42-C43	104 (7)	C81-C82-C83	116 (7)
C42-C43-C44	107 (7)	C82-C83-C84	101 (7)
C43-C44-N41	101 (8)	C83-C84-N81	107 (7)

determine the platinum oxidation state simply from the number of nitrate anions found in the crystal lattice. Further discussion about the platinum oxidation state of PPG is detailed in a later section of this paper together with the results of the magnetic susceptibility measurement.

Table V summarizes the geometric features of PPY, PPB, PPG, and PPT. In PPY and PPB the interior Pt–Pt bonds are longer than the terminal ones, while in PPT they are almost equal, and in PPG the relation is reversed. We still need more data to conclude whether this is a result of the increased oxidation state of platinum atoms or due to the effect that is specific to each amide ligand. The structural analyses of the PPB- or PPY-corresponding compounds of α-pyrrolidone would clarify that point. The tilt angle τ shows a slightly decreasing tendency as the platinum oxidation state is increased. This is a result of the shortening of the Pt–Pt bond as the platinum oxidation state is increased. Since

Table V. Geometric Comparison of Tetranuclear Platinum Compounds

compound	av Pt oxidn state	distance, Å			dihedral angle,[c] deg				ref
		Pt-Pt		Pt-L_{axial}	τ		ω		
cis-diammineplatinum α-pyridone yellow	2.0	2.88[a]			30.0		21		11
		3.13[b]							
cis-diammineplatinum α-pyridone blue	2.25	2.7745[a]		3.32 (NO_3^-)	27.4		21.7		8
		2.8870[b]					23.9		
cis-diammineplatinum α-pyrrolidone green	2.37	2.764[a]	2.761[a]	3.21 (NO_3^-)	24.5	26.9	0.8	0.8	present work
		2.739[b]	2.724[b]	2.95 (NO_3^-)	17.4	15.9	16.8	1.2	
		2.740[a]	2.753[a]				12.8	0.2	
							3.8	7.0	
cis-diammineplatinum α-pyrrolidone tan	2.5	2.70[a]		2.60 (NO_3^-)	18.7		4.1		10
		2.71[b]		2.72 (NO_3^-)	21.2		4.5		
		2.71[a]					5.0		
							5.1		

[a] Angles related to terminal Pt-Pt bonds. [b] Angles related to interior Pt-Pt bonds. [c] τ is the tilt angle between adjacent platinum coordination planes and ω is the torsion (or twist) angle about the Pt-Pt vector.

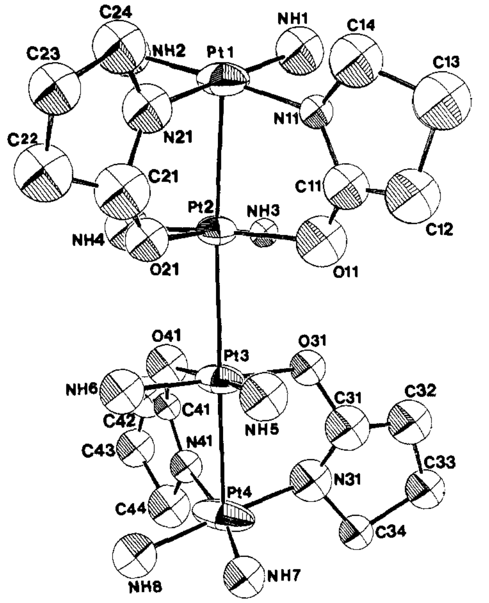

Figure 1. Structure of *cis*-diammineplatinum α-pyrrolidone green cation, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5.48+}$ The cation is actually a mixture of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$ and $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$ (see text for details). The thermal spheres are drawn with 50% probability.

the N(ring)···O(exocyclic) bite distance (about 2.3 Å) is shorter than the Pt–Pt distance, the tilt angle τ is decreased as the platinum oxidation state is increased and the Pt–Pt bond distance is decreased. The torsion angles ω about the Pt–Pt vector are about 22° for PPY and PPB. However, most of them are decreased to less than 10° in PPG and PPT. The two crystallographically independent cations are significantly different in their ω values. One cation has all four ω angles less than 10°, whereas two of the four ω values in the other cation are less than 5° and the remaining two are around 15°. Although the present analysis is not highly accurate because of the disorder mentioned above, the coordination spheres are definitely determined and no possibility seems to exist for the coordinating atoms to occupy more than one site. Accordingly, we consider the difference of the two independent cations is significant and is not due to the inaccuracy of the analysis.

No significant difference was observed in the platinum zigzag chain angles and Pt–O, Pt–N, and Pt–NH_3 bond lengths among the four tetranuclear platinum compounds. The coordination sphere of each platinum atom is almost planar. The shifts of each platinum atom from the least-squares planes are Pt1 0.01 Å, Pt2 0.07 Å, Pt3 0.43 Å, Pt4 0.02 Å, Pt5 0.02 Å, Pt6 0.003 Å, Pt7 0.04 Å, and Pt8 0.07 Å. As for α-pyrrolidone ligands, some of the C–C and C–N bond lengths may slightly deviate from the usual value; however, they would have no chemical significance in view of the fairly large standard deviations.

Table VI. Possible Hydrogen Bondings (Å) in the Crystal Lattice

NH3···OO8	2.84 (11)	OO24···OW5(i)	2.71 (23)
NH5···OO6	3.15 (7)	NH1···OO4(ii)	3.15 (9)
NH6···OO29	3.13 (16)	NH3···OO12(ii)	3.01 (15)
NH8···OO28	2.93 (17)	NH1···OO17(ii)	2.91 (16)
NH9···OO22	2.74 (8)	NH4···OO12(ii)	3.13 (17)
NH10···OO26	2.86 (14)	NH4···OO13(iii)	2.93 (13)
NH11···OO22	3.06 (10)	NH2···OO8(iv)	3.12 (13)
NH11···OO23	3.07 (12)	NH2···OO30(iv)	2.98 (12)
NH12···OO26	2.79 (17)	NH8···OO16(v)	3.21 (9)
NH13···OO21	3.09 (11)	NH10···OO24(v)	2.89 (9)
NH15···OO19	2.90 (15)	OO9···NH2(v)	3.01 (10)
OO4···NH1(i)	3.15 (9)	OO30···NH2(v)	2.98 (12)
OO12···NH3(i)	3.01 (15)	NH10···OO23(v)	3.06 (13)
OO17···NH1(i)	2.91 (16)	OO8···NH2(v)	3.12 (13)

[a] Roman numerals refer to the symmetry translations as follows: i $(1 + x, y, z)$, ii $(-1 + x, y, z)$, iii $(x, -1 + y, z)$, iv $(x, y, 1 + z)$, v $(x, y, -1 + z)$.

Table VI summarizes the possible hydrogen bondings in the crystal lattice. The axial coordination to platinum atoms at both ends of the chain is important in regard to the relation between the Pt–L_{axial} bond length and platinum oxidation state. Hollis et al. reported that axial coordination is favored and the Pt–L_{axial} bond distance is decreased with increasing platinum oxidation state, from a review of amidate-bridged dinuclear and tetranuclear compounds of platinum(II) and platinum(III).[17] However, in PPG no definite axial coordination was found. As Table III shows, only two loose coordination, Pt4–OO16 3.21 (9) Å and Pt8–OO1 2.95 (15) Å, were found, and no other significant coordination to platinum atoms at chain ends was found within 3.5-Å range. Accordingly, we cannot obtain any definite information about the platinum oxidation state. However, it is to be noted that both bond lengths, Pt–OO16 and Pt–OO1, are intermediate between those of PPB and PPT, which in accordance with the tendency of Pt–P bond lengths, also suggests an intermediate platinum oxidation state between 2.25 and 2.5.

Magnetic Susceptibility and Estimation of Average Platinum Oxidation State. A plot of the magnetic susceptibility χ_M', corrected for underlying diamagnetism and temperature-independent paramaganetism, vs. T is shown in Figure 2. The dependence of χ_M' on temperature fits a Curie–Weiss expression, $\chi_M' = C_T/(T - \theta)$. The Curie constant C_T and the Curie–Weiss constant, obtained from a least-square calculation, were 0.211 $cm^3\ kmol^{-1}$ and 0.961 K, respectively. The effective magnetic moment calculated from these values was 1.30 μ_B, which is significantly less than the value expected for the presence of one unpaired electron (1.73 μ_B). The magnetic susceptibility measurement of PPB shows that the temperature dependence of the magnetic susceptibility obeys the usual Curie–Weiss law and the effective

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(17) Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 6761–6763.

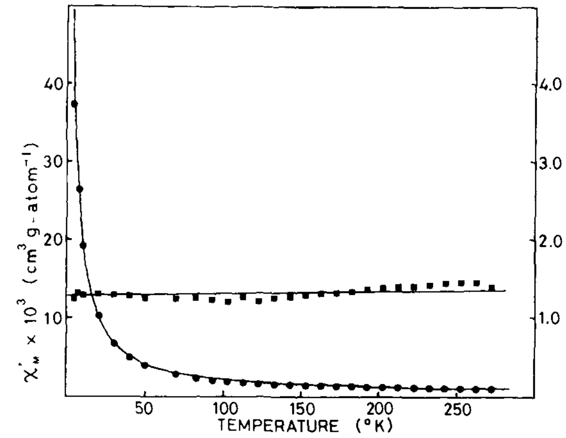

Figure 2. Temperature dependence of the magnetic susceptibility (●), χ_M', and effective magnetic moment (■), μ_e, per tetrameric unit of *cis*-diammineplatinum α-pyrrolidone green. Experimental data have been corrected for diamagnetism and temperature-independent paramagnetism.

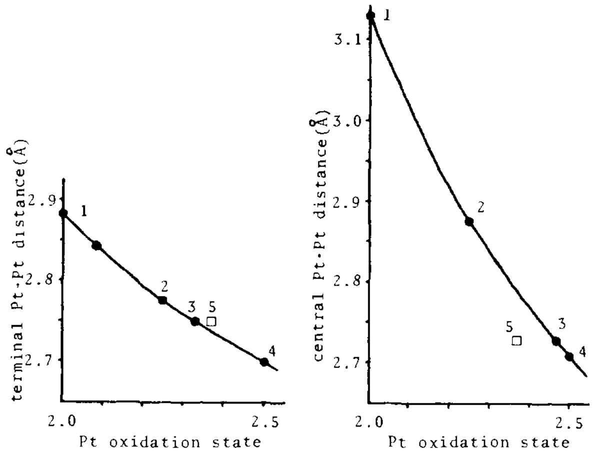

Figure 3. Relation of the Pt–Pt distance and the platinum oxidation state observed in platinum blue related tetranuclear platinum compouds. 1, *cis*-diammineplatinum α-pyridone yellow; 2, *cis*-diammineplatinum α-pyridone blue; 3, *cis*-diammineplatinum α-pyrrolidone green; 4, *cis*-diammineplatinum α-pyrrolidone tan; 5, ideal point for *cis*-diammineplatinum α-pyrrolidone green.

magnetic moment, 1.81 μ_B, is consistent with the presence of one unpaired electron per tetranuclear platinum unit with little interionic magnetic interaction in the crystal lattice.[8] On the other hand, our recent magnetic susceptibility measurement of PPT reveals it is almost diamagnetic.[10] Therefore, we consider that the low effective magnetic moment of PPG must be a result of the fact that PPG is, in fact, a mixture of the PPB-corresponding five-charged cation and the PPT-corresponding six-charged one. On this assumption, the low magnetic moment can be explained by the fact that PPG consists of a paramagnetic PPB-corresponding cation with an effective magnetic moment of 1.81 μ_B, diluted by diamagnetic PPT-corresponding cation. Therefore, the apparent magnetic moment, calculated per tetranuclear platinum unit, is less than 1.81 μ_B. On the basis of the measured effective magnetic moment of PPG, the existence ratios of both cations in PPG were calculated. The result is 52% for $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$ and 48% for $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$. From these values the average platinum oxidation state is calculated to be 2.37.

As mentioned in the previous section, the platinum oxidation state can also be inferred from the Pt–Pt bond lengths. Figure 3 shows the relation of the Pt–Pt bond length with the average platinum oxidation state in PPY, PPB, PPG, and PPT. The curves were determined from PPY, PPB, and PPT. Since the example of the tetranuclear platinum compounds is still scarce, it is yet difficult to tell which curve of the two is more reliable or more accurately reflects the platinum oxidation state. From the terminal Pt–Pt distance curve the average platinum oxidation state is determined to be 2.33, while from the interior Pt–Pt one it is 2.47. The former value is in good agreement with that calculated from the effective magnetic moment. However, more examples of this class of compounds are necessary to estimate accurately the platinum oxidation state. We currently adopt the average oxidation state of 2.37, based on the magnetic moment, and determine the formula of PPG as $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_{5.48}\cdot 3H_2O$. This is the first evidence of nonstoichiometry in this class of compounds, and we believe it would be helpful for the understanding of the properties of compounds under the generic name "platinum blue".

Acknowledgment. We are indebted to Prof. Y. Iidaka of the pharmaceutical faculty, University of Tokyo, for the use of the X-ray diffractometer, and also to Dr. T. Ohsawa of University of Tokyo, who kindly helped the authors measure the magnetic susceptibility. This work was financially supported by a grant (No. 23665) from the Japanese Ministry of Health and Welfare.

Registry No. $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_{5.48}\cdot 3H_2O$, 88657-27-6; *cis*-$(NH_3)_2PtCl_2$, 15663-27-1.

Supplementary Material Available: Listings of final thermal parameters and structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.