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A Tetranuclear Platinum Compound Containing Two Diamagnetically Coupled Platinum(III) Atoms: X-ray Structural Analysis of Bis[bis[μ-α-pyrrolidonato(1−)-N^2,O^2]bis[*cis*-diammineplatinum(II,III)]](*Pt*−*Pt*) Hexanitrate Dihydrate, $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O$

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The X-ray crystal structure has been determined for a dark brownish red crystal, *cis*-diammineplatinum α-pyrrolidone tan, or bis[bis[μ-α-pyrrolidonato(1−)-N^1,O^2]bis[*cis*-diammineplatinum(II,III)]](*Pt*−*Pt*) hexanitrate dihydrate, $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O$. The crystal is monoclinic, space group $P2_1/c$, with cell dimensions a = 14.960 (81) Å, b = 16.254 (7) Å, c = 19.164 (96) Å, and β = 115.10 (37)°, and has four formula units in the cell. The structure was determined by standard methods and refined to R_1 = 0.126 and R_2 = 0.119 on the basis of 3435 independent reflections. The cation has turned out to be a tetranuclear chain structure, whose neighboring platinum atoms are bridged by exocyclic oxygen atoms and deprotonated nitrogen atoms of the α-pyrrolidone ligands. The structure is basically the same as that of the recently reported blue compound, *cis*-diammineplatinum α-pyridone blue, or bis[bis[μ-α-pyridonato(1−)-N^1,O^2]bis[*cis*-diammineplatinum(II,III)]](*Pt*−*Pt*) pentanitrate hydrate, $[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_5\cdot H_2O$. However, the average oxidation state of the platinum atoms in the present compound is +2.5, whereas that of the latter is +2.25. The oxidation state for the present compound has also been confirmed by oxidative titration using Ce^{IV}. Magnetic susceptibility measurement of the title compound indicates that the compound is diamagnetic and the cation consists of two Pt^{II} and two Pt^{III} atoms. Since X-ray analysis shows that the two platinum dimers, whose platinum atoms are amidate bridged, in the tetranuclear chain are almost equivalent, the two unpaired electrons seem to be strongly diamagnetically coupled and are delocalized over the four platinum atoms.

Introduction

A class of dark blue platinum compounds, so-called "platinum blues", have attracted interest of chemists and physicians, since, in the course of study on the interactions of DNA bases with antitumor-active *cis*-dichlorodiammineplatinum(II), the resulting blue material, "platinum pyrimidine blues", proved to exhibit high antitumor activities and low associated nephrotoxicities.[1-4] These compounds exhibit abnormally deep blue color[5] and paramagnetic and mixed-valent oligomeric nature.[1-8] These facts also make the compounds very intriguing simply as a subject of coordination chemistry, apart from their antitumor activities. Although platinum blue was first reported as "platinblau" as early as 1908,[5] their structures and formulas have long been unknown, because they are unstable in solution and difficult to synthesize reproducibly. They are highly soluble in water and had never been obtained as crystals.[5-8]

Recently, Barton et al. first reported the synthesis of crystalline *cis*-diammineplatinum α-pyridone blue (PPB), bis[bis[μ-α-pyridonato(1−)-N^2,O^2]bis[*cis*-diammineplatinum(II,III)]](*Pt*−*Pt*) pentanitrate hydrate, $[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_5\cdot H_2O$, and solved the structure by X-ray analysis.[9,10] The compound has turned out to consist of a tetranuclear chain cation, whose neighboring platinum atoms are amidate bridged. Three of the platinum atoms are formally in the oxidation state of +2, and the remaining one is +3; that is, the average oxidation state is +2.25, although the four platinum atoms are actually rather equivalent and the one unpaired electron is delocalized over the four platinum atoms.[10]

On the other hand, we have reently obtained a crystalline dark brownish red compound, *cis*-diammineplatinum α-pyrrolidone tan (PPT),[11] bis[bis[μ-α-pyrrolidonato(1−)-N^2,O^2]bis[*cis*-diammineplatinum(II,III)]](*Pt*−*Pt*) hexanitrate dihydrate. Platinum tans have been reported to be obtained unexpectedly during the preparation of platinum blues.[13] It is also reported that their appearance is due to the existence of a small amount of chloride ion from the starting material *cis*-$(NH_3)_2PtCl_2$, which should have to be removed completely as AgCl before amide ligand is added to the platinum solution.[14] There is another report that platinum tans are reaction products of platinum blues with nitric acid[6] or hydrochloric acid.[15] In addition to these observations, it is known that their colors change sometimes to green or violet, whose origin is still unknown.[6,8] These facts, together with their controversial magnetic properties,[5,6,13,16] reflect their complicated behavior in solution, difficulty in isolating the pure species, and difficulty in reproducing the synthesis.

In this paper, we report the crystal structure and magnetic property of *cis*-diammineplatinum α-pyrrolidone tan (PPT). The structure of the cation and the oxidation state of the platinum atoms are compared with those of closely related *cis*-diammineplatinum α-pyridone blue (PPB).

Experimental Section

Preparation of the compound has been reported previously.[11] The crystal is very brittle, and it is very difficult to obtain crystals suitable for X-ray diffraction analysis. The Weissenberg photographs exhibited diffuse reflections. Both photographs of a^*b^* and b^*c^* planes exhibit streak lines in the b^* direction, indicating possible random arrangement of atoms in different cells in the b direction.[12]

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[16] The original platinblau was diamagnetic;[5] however, recently it is reported to be paramagnetic.[13]

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Table I. Crystal Data (at 22 °C) and Experimental Conditions for the X-ray Intensity Measurement of *cis*-Diammineplatinum α-Pyrrolidone Tan

compd: $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$
cryst syst: monoclinic
space group: $P2_1/c$
$a = 14.960\ (81)$ Å
$b = 16.254\ (7)$ Å
$c = 19.164\ (96)$ Å
$\beta = 115.10\ (37)°$

$V = 4220.0$ Å^3
mol wt = 1661.2
$Z = 4$
ρ(obsd) = 2.64 g cm^{-3}
ρ(calcd) = 2.62 g cm^{-3}
$\mu = 140.18$ cm^{-1}

instrumetn: Philips PW 1100
radiation: Mo Kα (λ = 0.7107 Å), graphite monochromatized
takeoff angle: 2.0°
detector aperture: 6 × 6 mm
scan mode: ω–2θ
scan width: $\omega = 1.2 + 0.3 \tan\theta$
2θ limit: $3° < 2\theta < 55°$
scan rate: 2.0°/min in 2θ
transmissn factors: 0.07–0.17
bkgd measurements: stationary crystal, stationary counter; measurement time = (scan time)$/2(I_{\text{bck}}/I_{\text{int}})^{1/2}$, where I_{bck}(counts/s) is average value preliminarily measured at both scan ends and I_{int}(counts/s) is the value of the peak
stds: three reflcns measd every 2 h showed random, statistical fluctuations
no. of reflcns collcd: 4673
no. of reflcns used for calculation: 3435 unique reflcns for which $|F_o| > 3\sigma|F_o|$
computer programs used: local version of UNICS (Sakurai, 1967) and ORTEP (Johnson, 1965)

Collection of X-ray Data. Preliminary Weissenberg photographs of the crystal showed it is monoclinic. Unit cell parameters were obtained from least-squares fit of 20 reflections in the range of $20° < 2\theta < 35°$ measured on a Philips PW1100 diffractometer using graphite-monochromated Mo Kα radiation. Crystal data and other information related to the data collection are summarized in Table I. Density was measured by flotation in a bromoform–chloroform mixture. Intensities were measured with the ω–2θ scan technique and corrected for Lorentz–polarization effects and absorption.

Solution of the Structure. The coordinates of the four platinum atoms were found from a three-dimensional Patterson map, and a series of block-diagonal least-squares refinements followed by three-dimensional Fourier synthesis revealed all the O, N, and C atoms in the α-pyrrolidonate and ammine ligands. After further refinement of the coordinates with anisotropic temperature factors for platinum atoms and isotropics for other elements, a difference synthesis was calculated and all the nitrate anions and waters of crystallization were located. No attempt was made to locate the hydrogen atoms. The structure was finally refined with anisotropic temperature factors for platinum atoms and isotropics for other elements to the final discrepancy index of $R_1 = 0.126$ and $R_2 = 0.119$, 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 refinement with anisotropic temperature factors for all the atoms was also attempted. Although a decrease of about 0.01 was observed in R value, some of the final temperature factors were unusually low values, which is probably the result of the disorder that is not included in the calculation or inadequate absorption correction. Therefore, we abandoned the anisotropic temperature factors for C, N, and O and refined these atoms isotropically in the final calculation. The weight of each reflection was determined as $w_i = 1/\sigma^2(F_o)$. Atomic scattering factors were taken from ref 17, and the anomalous dispersion corrections were based on ref 18.

Table II. Final Positional Parameters[a]

atom	x	y	z
Pt1	−0.1340 (4)	0.2325 (2)	0.1609 (2)
Pt2	0.0625 (2)	0.2320 (2)	0.2015 (2)
Pt3	0.2512 (4)	0.2387 (2)	0.2175 (2)
Pt4	0.4485 (3)	0.2502 (2)	0.2630 (2)
N1	−0.1473 (96)	0.1206 (71)	0.2090 (65)
N2	−0.1473 (44)	0.3008 (29)	0.2524 (26)
N3	0.0811 (59)	0.1122 (39)	0.2556 (37)
N4	0.0958 (98)	0.3047 (74)	0.2933 (66)
N5	0.2179 (66)	0.1366 (44)	0.1445 (42)
N6	0.1916 (51)	0.3050 (36)	0.1102 (32)
N7	0.4704 (60)	0.1345 (40)	0.2129 (37)
N8	0.4487 (64)	0.3318 (44)	0.1722 (41)
N11	−0.1481 (57)	0.1692 (38)	0.0650 (36)
C12	−0.0659 (65)	0.1541 (50)	0.0507 (42)
O12	0.0295 (45)	0.1771 (29)	0.0953 (27)
C13	−0.0891 (82)	0.1090 (57)	−0.0192 (54)
C14	−0.2117 (94)	0.0963 (73)	−0.0560 (70)
C15	−0.2298 (97)	0.1458 (74)	−0.0053 (71)
N21	−0.1188 (46)	0.3431 (30)	0.1125 (28)
C22	−0.0368 (76)	0.3848 (51)	0.1248 (49)
O22	0.0479 (40)	0.3438 (25)	0.1503 (23)
C23	−0.0613 (91)	0.4580 (75)	0.0734 (69)
C24	−0.1573 (90)	0.4760 (69)	0.0556 (65)
C25	−0.1999 (71)	0.3889 (48)	0.0629 (45)
N31	0.4351 (13)	0.1999 (8)	0.3573 (3)
C32	0.3590 (69)	0.1465 (47)	0.3465 (43)
O32	0.2659 (36)	0.1722 (22)	0.3170 (21)
C33	0.3746 (93)	0.1342 (73)	0.4353 (70)
C34	0.4786 (96)	0.1140 (66)	0.4591 (63)
C35	−0.5151 (93)	0.1768 (70)	0.4180 (64)
N41	0.4364 (37)	0.3585 (29)	0.3246 (27)
C42	0.3444 (65)	0.3731 (41)	0.3052 (37)
O42	0.2566 (36)	0.3470 (24)	0.2713 (21)
C43	0.3779 (88)	0.4497 (59)	0.3344 (56)
C44	0.4703 (90)	0.4637 (72)	0.3984 (68)
C45	0.5191 (78)	0.4021 (53)	0.3684 (51)
N9	0.0274 (87)	0.1770 (62)	0.4221 (57)
OO1	−0.0119 (66)	0.1557 (47)	0.3580 (43)
OO2	0.0028 (93)	0.1814 (66)	0.4712 (61)
OO3	0.1127 (86)	0.1654 (62)	0.4458 (57)
N10	0.6589 (91)	0.4512 (52)	0.2225 (55)
OO4	0.6413 (58)	0.3816 (35)	0.2054 (37)
OO5	0.7513 (59)	0.4652 (42)	0.2450 (38)
OO6	0.6266 (46)	0.4971 (29)	0.2485 (27)
N11	0.7227 (106)	0.2446 (92)	0.3627 (75)
OO7	0.6456 (58)	0.2641 (47)	0.3054 (37)
OO8	0.6505 (42)	0.2320 (32)	0.3702 (26)
OO9	0.8099 (16)	0.2247 (20)	0.4031 (5)
N12	0.6926 (73)	0.0170 (52)	0.3389 (47)
OO10	0.7794 (64)	0.0003 (45)	0.3674 (41)
OO11	0.6769 (68)	0.0877 (48)	0.3182 (45)
OO12	0.6591 (78)	−0.0374 (54)	0.3682 (50)
N13	−0.0241 (72)	−0.0538 (50)	0.1615 (45)
OO13	−0.0137 (68)	−0.1078 (45)	0.1236 (44)
OO14	0.0005 (70)	0.0001 (49)	0.1229 (46)
OO15	0.0030 (74)	−0.0266 (51)	0.2228 (45)
N14	0.4103 (67)	0.7194 (50)	0.4018 (43)
OO16	0.3233 (65)	0.7200 (48)	0.3810 (43)
OO17	0.4854 (62)	0.7512 (51)	0.4306 (41)
OO18	0.4703 (82)	0.6648 (61)	0.4001 (56)
OW1	0.6474 (65)	0.1657 (45)	0.1751 (40)
OW2	0.2964 (56)	0.3216 (38)	0.4391 (35)

[a] Estimated standard deviations are given in parentheses.

In the final difference map, some residual electron density peaks were observed between the neighboring platinum atoms and also at both ends of the platinum zigzag chain structure (see Figure 1). We carefully considered a possibility of disorder where some of the platinum atoms are displaced in the direction of the chain vector. If the residual peaks really mean random arrangement of platinum atoms in the chain direction, the disorder corresponds to be in *ac* plane, since the platinum chains lie in *ac* plane (see Table II). However, since the residual electron densities are only about 5% that of a platinum atom and the Weissenberg photographs show, as mentioned earlier, a disorder of *b*-axis direction, that is, perpendicular to the zigzag chains, we conclude that these residual peaks are probably the result of an inadequate absorption correction. We also attempted to contrive models for the random arrangement in *b*-axis direction; however, other residual peaks were so small that no significant arrangement could be obtained from the final difference map.

The final non-hydrogen atomic positional parameters are listed in Table II. The final thermal parameters and the observed and calculated structure factors are available as Tables S1 and S2, supplementary material.

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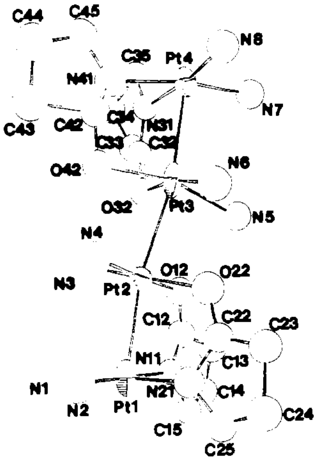

Figure 1. Structure of the *cis*-diammineplatinum α-pyrrolidone tan cation, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$. The thermal ellipsoids are drawn with 50% probability.

Table III. Interatomic Distances (Å) within the Cation and Nitrate Anions[a]

	Coordination Sphere		
Pt1-Pt2	2.702 (6)	Pt1-N1	2.09 (14)
Pt2-Pt3	2.710 (5)	Pt1-N2	2.16 (5)
Pt3-Pt4	2.706 (6)	Pt1-N11	2.08 (7)
Pt2-N3	2.17 (7)	Pt1-N21	2.08 (5)
Pt2-N4	2.00 (16)	Pt3-N5	2.09 (8)
Pt2-O12	2.08 (5)	Pt3-N6	2.15 (5)
Pt2-O22	2.03 (4)	Pt3-O32	2.12 (3)
Pt4-N7	2.20 (8)	Pt3-O42	2.02 (3)
Pt4-N8	2.19 (8)	Pt1-OO16	2.60 (1)
Pt4-N31	2.07 (1)	Pt4-OO7	2.72 (1)
Pt4-N41	2.17 (5)		
	Pyrrolidone Rings		
O12-C12	1.37 (11)	O22-C22	1.33 (12)
C12-C13	1.44 (15)	C22-C23	1.49 (18)
C13-C14	1.68 (18)	C23-C24	1.36 (19)
C14-C15	1.37 (19)	C24-C25	1.58 (17)
C15-N11	1.43 (17)	C25-N21	1.40 (11)
N11-C12	1.39 (12)	N21-C22	1.33 (12)
O32-C32	1.33 (10)	O42-C42	1.27 (10)
C32-C33	1.63 (17)	C42-C43	1.37 (15)
C33-C34	1.46 (17)	C43-C44	1.42 (19)
C34-C35	1.53 (19)	C44-C45	1.49 (18)
C35-N31	1.32 (10)	C45-C41	1.36 (12)
N31-C32	1.38 (14)	N41-C42	1.29 (11)
	Nitrate Anions		
N9-OO1	1.17 (15)	N10-OO4	1.18 (15)
N9-OO2	1.15 (18)	N10-OO5	1.28 (15)
N9-OO3	1.17 (17)	N10-OO6	1.12 (14)
N11-OO7	1.24 (17)	N12-OO10	1.21 (13)
N11-OO8	1.16 (16)	N12-OO11	1.21 (14)
N11-OO9	1.25 (14)	N12-OO12	1.26 (15)
N13-OO13	1.19 (14)	N14-OO16	1.19 (13)
N13-OO14	1.30 (15)	N14-OO17	1.15 (13)
N13-OO15	1.16 (14)	N14-OO18	1.27 (15)

[a] Estimated standard deviations are given in parentheses.

Oxidative Titration. The titration was monitored potentiometrically

Oxidative Titration. The titration was monitored potentiometrically by using platinum vs. AgCl electrodes. The titrant was Ce^{IV} and was prepared by dissolving ammonium cerium(IV) sulfate in 0.72 N sulfuric acid to the concentration of 6.1×10^{-3} N. About 0.01 g of PPT was weighed and dissolved in 40 mL of 0.1 N nitric acid. Both the titrand and the titrant were degassed with argon before titration and were also protected from the air by argon flow during the titration.

Magnetic Susceptibility Measurement. A PAR Model 150A vibrating-sample magnetometer was used to measure the magnetic susceptibility. a powdered sample was placed in a container on the tip of the vibrating rod. The susceptibility was measured at room temperature and at liquid-nitrogen and liquid-helium temperatures.

Table IV. Interatomic Bond Angles (deg) within the Cation[a]

	Coordination Sphere		
Pt1-Pt2-Pt3	170.4 (1)	Pt2-Pt3-Pt4	168.8 (1)
N1-Pt1-N2	92 (5)	N3-Pt2-N4	100 (6)
N1-Pt1-N11	88 (5)	N3-Pt2-O12	91 (4)
N1-Pt1-N21	179 (5)	N3-Pt2-O22	179 (4)
N2-Pt1-N11	170 (4)	N4-Pt2-O12	169 (6)
N2-Pt1-N21	89 (3)	N4-Pt2-O22	80 (4)
N11-Pt1-N21	91 (4)	O12-Pt2-O22	89 (5)
N5-Pt3-N6	83 (4)	N7-Pt4-N8	97 (4)
N5-Pt3-O32	96 (5)	N7-Pt4-N31	98 (3)
N5-Pt3-O42	168 (5)	N7-Pt4-N41	174 (4)
N6-Pt3-O32	163 (5)	N8-Pt4-N31	165 (3)
N6-Pt3-O42	88 (4)	N8-Pt4-N41	88 (4)
O32-Pt3-O42	91 (4)	N31-Pt4-N41	78 (3)
	Pyrrolidone Rings		
Pt1-N11-C12	120 (6)	Pt1-N21-C22	129 (8)
Pt1-N11-C15	135 (7)	Pt1-N21-C25	123 (5)
Pt2-O12-C12	119 (6)	Pt2-O22-C22	121 (5)
C12-N11-C15	104 (9)	C22-N21-C25	109 (8)
O12-C12-N11	127 (6)	O22-C22-N21	118 (6)
O12-C12-C13	120 (8)	O22-C22-C23	125 (7)
N11-C12-C13	113 (8)	N21-C22-C23	110 (8)
C12-C13-C14	104 (7)	C22-C23-C24	106 (8)
C13-C14-C15	98 (9)	C23-C24-C25	102 (8)
C14-C15-N11	118 (9)	C24-C25-N21	106 (6)
Pt4-N31-C32	120 (4)	Pt4-N41-C42	109 (5)
Pt4-N31-C35	120 (4)	Pt4-N41-C45	120 (6)
Pt3-O32-C32	104 (3)	Pt3-O42-C42	111 (3)
C32-N31-C35	110 (6)	C42-N41-C45	131 (8)
O32-C32-N31	121 (3)	O42-C42-N41	147 (5)
O32-C32-C33	98 (6)	O42-C42-C43	129 (6)
N31-C32-C33	100 (6)	N41-C42-C43	84 (7)
C32-C33-C34	91 (8)	C42-C43-C44	123 (7)
C33-C34-C35	105 (9)	C43-C44-C45	91 (7)
C34-C35-N31	105 (6)	C44-C45-N41	97 (7)

[a] Estimated standard deviations are in parentheses.

Results and Discussion

Description of the Structure. The structure of the cation and the atomic-numbering schemes are depicted in Figure 1. The interatomic distances and bond angles within the cation are listed in Tables III and IV, respectively.

The cation, $[Pt_4(NH_3)_8(C_4H_6NO_4)]^{6+}$, consists of a tetranuclear platinum chain, which comprises two dimers of platinum atoms linked through amidate bridges. Each platinum atom in the dimer is cis coordinated with two ammine ligands and either two exocyclic oxygen atoms or two deprotonated ring nitrogen atoms of the α-pyrrolidone ligands. Therefore, these dimers have the so-called head-to-head orientation.[19] The two dimers constitute the tetranulcear chain cation in an orientation that the platinum atoms, coordinated to exocyclic oxygens, would be the inner two of the tetranuclear chain. The bonding of the two dimers is due to partial metal-metal bonding and probably also to hydrogen bonding between the hydrogen atoms of the ammine ligands and exocyclic oxygen atoms. The structure of the cation is, except for the difference of the ligands, basically similar to that of PPB.[10] However, the charge of the cation is different. Both the elemental analysis[20] and the present X-ray analysis, where six nitrate anions have been located, show that the cation is hexavalent, whereas the charge of the cation in PPB is 5+. Therefore, the average platinum oxidation state of PPT is +2.5, which formally corresponds to two Pt(III) and two Pt(II) or three Pt(II) and one Pt(IV) in the tetranuclear chain. This average oxidation state of the platinum atoms has been confirmed by oxidative titration as mentioned in a later section. PPT would be the first platinum complex whose platinum

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

(20) Anal. Calcd: C, 11.44; H, 3.16; N, 15.18; Pt, 46.97. Found: C, 11.24; H, 3.09; N, 14.70; Pt, 46.1.

Table V. Selected Geometric Features of *cis*-Diammineplatinum α-Pyrrolidone Tan

plane 1	plane 2	dihedral angle, deg
Pt1 coord plane	Pt2 coord plane	18.7
Pt2 coord plane	Pt3 coord plane	1.0
Pt3 coord plane	Pt4 coord plane	21.2
Pt1-Pt2-N1	Pt1-Pt2-N3	1.9
Pt1-Pt2-N2	Pt1-Pt2-N4	4.5
Pt2-Pt3-N3	Pt2-Pt3-N5	63.5
Pt2-Pt3-N4	Pt2-Pt3-N6	66.7
Pt3-Pt4-N5	Pt3-Pt4-N7	8.4
Pt3-Pt4-N6	Pt3-Pt4-N8	5.1
Pt1-Pt2-O12	Pt1-Pt2-N11	4.9
Pt1-Pt2-O22	Pt1-Pt2-N21	1.8
Pt3-Pt4-O32	Pt3-Pt4-N31	7.5
Pt3-Pt4-O42	Pt3-Pt4-N41	4.9

average oxidation state is +2.5.[21] Regarding the average oxidation state of platinum atoms, it should also be noted that recently Hollis et al. reported a greenish yellow tetranuclear platinum compound, *cis*-diammineplatinum α-pyridone yellow (PPY), bis[bis[μ-α-pyrrolidonato(1−)-N^1,O^2]bis[*cis*-diammineplatinum(II)]](*Pt–Pt*), $[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_4$, whose structure is also similar to those of PPT or PPB, but the average platinum oxidation state is +2.0.[19] These facts reveal the characteristic nature of this class of compounds that the platinum oxidation state can be changed various degrees without basic structural change.

There are also some distinct differences in the backbone structures of PPB and PPT cations. The Pt–Pt distances in PPT is significantly shorter than those of PPB. It has already been established for one-dimensional metal-chain complexes that the metal-metal bond distance is correlated with the formal oxidation state of the metal. Similar relation is also reported for platinum complexes having bridging ligands.[10] The Pt–Pt distances in PPT are, as shown in Table III, intermediate between those observed in PPB (platinum average oxidation state +2.25) and ligand-bridged dimer complexes of Pt(III). The Pt–Pt distances of PPB are 2.7745 (4) and 2.8770 (5) Å, whereas the Pt(III)–Pt(III) distances are 2.466 Å in the sulfate-bridged dimer $K_2[Pt_2(SO_4)_4(H_2O)_2]$,[26] 2.486 (2) Å in $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$,[27] 2.471 (1) Å in $K_2[Pt_2(SO_4)_4(OSMe_2)_2]{\cdot}4H_2O$,[27] 2.539 (1) Å in the α-pyridone-bridged platinum(III) dimer $[Pt_2(NH_3)_4(C_5H_4NO)_2(NO_3)(H_2O)](NO_3)_3{\cdot}2H_2O$,[23] and 2.557 (1) Å in the trifluoroacetate-bridged platinum(III) dimer $[(Mepy)(CH_3)_2Pt(O_2CCF_3)_2Pt(CH_3)_2(Mepy)]$, where Mepy = 4-methylpyridine.[28] These facts also support the assignment of +2.5 to the average oxidation state of the platinum atoms in PPT. It should also be noticed that the bridged Pt–Pt bonds, Pt1–Pt2 and Pt3–Pt4, are only slightly longer (0.01 Å) than the central nonbridged Pt2–Pt3 distance, which is in contrast to the fact that, in PPB, both bridged Pt–Pt bonds are 0.1 Å shorter than the central nonbridged Pt–Pt bond, and this has been considered to be due to the presence of bridging ligands.[10] Although more experimental data are required for this class of tetranuclear platinum complexes to conclude a correlation between the platinum oxidation state and the Pt–Pt distance, the present study may indicate that the bridged and nonbridged Pt–Pt distances approach being equal to each other, as well as becoming shorter, as the average oxidation state is increased.

Table VI. Hydrogen Bondings (Å) in the Crystal Lattice[a]

N1---OO1	2.77	N4---OO13(iii)	2.78
N1---OW1(ii)	2.95	N4---OO15(iii)	3.06
N1---OO16(v)	2.94	N4---OW2	3.12
N2---OO1	3.20	N7---OW1	3.06
N2---OO5(ii)	3.04	N7---OO11	2.98
N2---OO4(ii)	3.18	N8---OO7	3.16
N2---OO13(iii)	2.96	N8---OO4	2.79
N2---OO16 (v)	3.07	OO17---N8(iv)	2.86
N3---OO14	2.94	OO18---N7(iv)	2.71
N3---OO1	2.93	OO6---N7(iv)	2.92

[a] Roman numerals refer to the symmetry translations as follows: (i) $1 + x, y, z$, (ii) $-1 + x, y, z$, (iii) $-x, 0.5 + y, 0.5 - z$, (iv) $1 - x, 0.5 + y, 0.5 - z$, (v) $-x, -0.5 + y, 0.5 - z$.

Table V summarizes the dihedral angles between major planes that characterize the structure of the cation. All the angles between adjacent platinum coordination planes are comparable to those in PPB. However, the angles between the planes Pt1–Pt2–N1 and Pt1–Npt2–N3, Pt1–Pt2–N2 and Pt1–Pt2–N4, Pt3–Pt4–N5 and Pt3–Pt4–N7, and Pt3–Pt4–N6 and Pt3–Pt4–N8 are all less than 10°, which are distinctively different from those of PPB or PPY. The dihedral angles in the latter two compounds are about 22°.[19] This means that the corresponding ammine ligands coordinated to adjacent platinum atoms are, if looked at from the direction of the Pt–Pt vector, staggered, or in another expression, the Pt–Pt bonding is twisted in these compounds, while the twist is little in the present compound PPT. The reason for this difference is at the moment unknown. In PPT the dihedral angles between the planes determined by the ammine nitrogen atoms and the Pt2–Pt3 bond are also considerably different from those of PPB and PPY. In the latter two compounds, the inversion center is located at the middle of the Pt2–Pt3 vector and, accordingly, the dihedral angle between the planes Pt2–Pt3–N3 and Pt2–Pt3–N5 and that of Pt2–Pt3–N4 and Pt2–Pt3–N6 are strictly equal, 89°. Therefore, in this respect, the basic twist angles around the platinum tetranuclear chain is distinctively different between the present compound PPT and the previously reported PPB and PPY.[9]

It is also noteworthy that the platinum atoms at both ends of the chain are loosely coordinated by oxygen atoms of nitrate groups; Pt1–OO16 = 2.603 (10) Å and Pt4–OO7 = 2.715 (10) Å. These distances are intermediate between that of PPB[10] (3.321 (9) Å) and those of the recently reported α-pyridone-bridged Pt(III) dimer[23] (2.17 Å in $[(NO_3)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(NO_3)]^{2+}$). Considering the fact that axial coordination is favored as the platinum oxidation state is increased, it seems that the present intermediate Pt–O(NO_3) distance also supports the average oxidation state of +2.5 in PPT.

The Pt1–Pt2–Pt3 and Pt2–Pt3–Pt4 angles are 170.4 (1) and 168.8 (1)°, respectively, and are almost comparable to those of PPB.[10] The Pt–O and Pt–N bond lengths within the coordination spheres of each platinum atom do not differ significantly from those reported for PPB (Table III). The coordination sphere of each platinum atom is almost planar. The shifts of each platinum atom from the plane are as follows: Pt1, 0.09 Å; Pt2, 0.02 Å; Pt3, 0.2 Å; Pt4, 0.003 Å. Pt1 and Pt2 are displaced in the opposite direction from one another in the bridged dimer, while, in the other bridged dimer, Pt3 is fairly largely displaced from the coordination plane to approach Pt2 and Pt4 is almost in the coordination plane. Some

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(21) Although Faggiani et al. have reported the preparation and the crystal structure of a deep yellow bis(μ-1-methylcytosinato-N^3,N^4)bis(*cis*-nitrodiammineplatinum)(*Pt–Pt*) dinitrate, whose platinum atoms are reportedly in the average oxidation state of +2.5 (see ref 22), the assignment of this oxidation state needs confirmation by another method. The relation of Pt–Pt distance and Pt oxidation state suggests that this compound exists rather as a Pt(III) complex (see ref 23).

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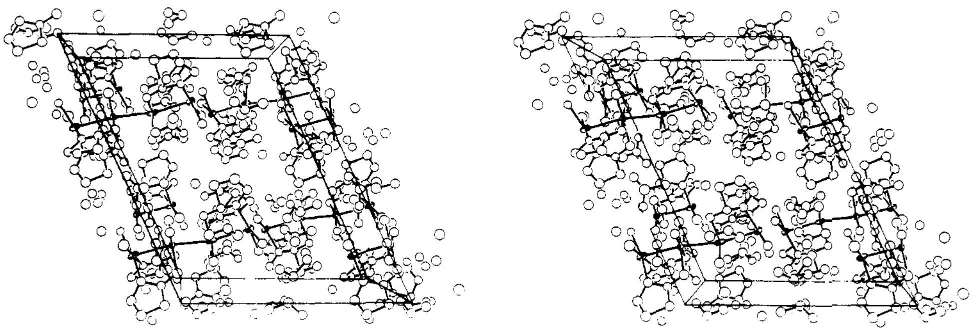

Figure 2. Stereoscopic view of the crystal structure of *cis*-diammineplatinum α-pyrrolidone tan, $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O$. The view is along the *b* axis, and the thermal ellipsoids are drawn with 30% probability. The *a* axis is parallel to the bottom of the page.

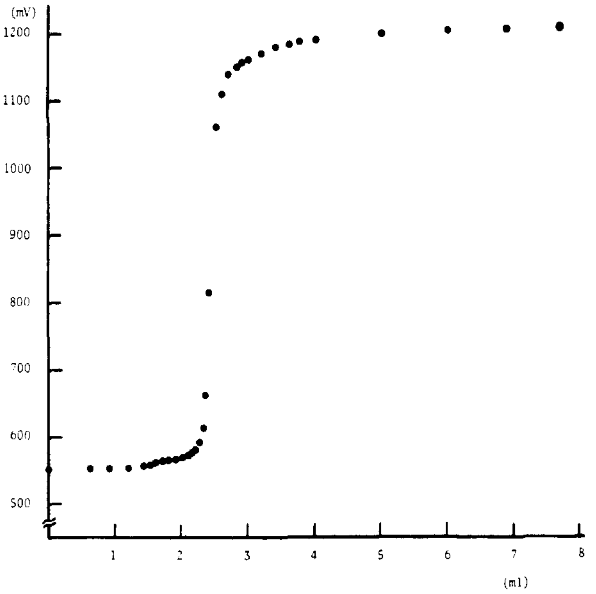

Figure 3. Titration curve of PPT (~0.01 g) with 6.1×10^{-3} N Ce^{IV} in 0.1 N HNO_3.

of the C–C or C–N bond lengths in the α-pyrrolidonate ligands show slight deviation from the usual values, which however would have no chemical significance in view of the fairly large standard deviations.

There is no significant interaction between neighboring cations. The capping nitrate anions do not coordinate to other cations but rather occupy the vacancies in the crystal lattice with little significant interaction with other cations, anions, or water molecules. Table VI summarizes the hydrogen bonding in the crystal lattice. The crystal packing is shown in Figure 2. Although the final *R* value is relatively high, Pt–Pt distances and Pt–coordinating atom distances, together with the results of the following oxidative titration and magnetic susceptibility measurement, strongly support the analysis of the structure and the assignment of the oxidation state.

Oxidative Titration and Magnetic Susceptibility. The result of the potentiometric oxidative titration with Ce^{IV} in 0.1 N HNO_3 is shown in Figure 3, which shows one end point corresponding to the change $Pt^{2.5} \rightarrow Pt^{III}$. This result confirms the present assignment of the average platinum oxidation state of +2.5. It is reported that a similar titration of PPB with Ce^{IV} in 4.5 N HCl[13] shows two successive end points corresponding to $Pt^{2.25} \rightarrow Pt^{III}$ and $Pt^{III} \rightarrow Pt^{IV}$, respectively. However, in our experiment, no second end point corresponding to $Pt^{III} \rightarrow Pt^{IV}$ was observed. This difference may come from the difference of the acid used. In the presence of a small amount of chloride ion, PPB solution turns a brownish color rather than blue, although chloride ion itself is a poor reducing or oxidizing agent and is unlikely to affect the average oxidation state of platinum atoms.[14] It is highly possible that the chemical species are different in 4.5 N HCl and 0.1 N HNO_3 and, therefore, the oxidation reaction differs in these two acids. We also attempted, for comparison, to carry out the titration in hydrochloric acid solution; however, this acid makes stable voltage reading impossible and we therefore abandoned the titration in this acid. Although the second end point was not observed in the present study, it is very unlikely that the average oxidation state is +3.5, considering the Pt–Pt distance of PPT.

The magnetic susceptibility measurement shows PPT is diamagnetic with χ_M of -1.7×10^{-3} cm^3 mol^{-1} both at liquid-N_2 and at room temperatures, although it gives a very slight ESR signal.[29] Considering the fact that the three Pt–Pt bond lengths are almost equivalent and there is no special bonding whose length is smaller than the others, PPT is essentially very slightly paramagnetic and the two unpaired electrons from the two Pt(III) atoms are strongly coupled diamagnetically and delocalized over the four platinum atoms, rather than forming a metal–metal bond between the two Pt(III) atoms. The possibility that one Pt(IV) atom exists in the tetranuclear chain is also excluded considering the equivalency of the four platinum atoms. In the oxidative titration of PPB in 0.05 HNO_3 with Ce^{IV}, monitored by ESR peak height of $g_\perp$ and visible absorption at 680 nm, PPB is directly oxidized presumably to two diamagnetic Pt(III) dimers.[14] This means that no intermediate corresponding to PPT is produced by this oxidation, which is very suggestive from the viewpoint of the formation pathway of PPT. The oxidative titration suggests that PPT is produced probably from the dimers containing Pt(III), rather than by the oxidation of the corresponding blue tetranuclear cation of $Pt^{2.25}$.

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Registry No. $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O$, 80612-41-5.

Supplementary Material Available: Final temperature parameters (Table S1) and observed and calculated structure factors (Table S2) (21 pages). Ordering information is given on any current masthead page.

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(29) We considered the possibility of the existence of paramagnetic impurity. However, a very small ESR signal always appeared and did not differ from batch to batch. Therefore, we have concluded it is intrinsic in the nature of PPT. Details of the ESR spectrum will be published elsewhere.