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Crystal Structure of Nonstoichiometric Tetranuclear Platinum Compound, *cis*-Diammineplatinum α-Pyrrolidone Violet, $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_2(NO_3)_{2.56}\cdot 5H_2O$

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Nonstoichiometric platinum tetranuclear compound, *cis*-Diammineplatinum α-Pyrrolidone Violet, $[Pt_4(NH_3)_8(C_4H_6NO)_4)(PF_6)_2(NO_3)_{2.56}\cdot 5H_2O$, has been synthesized and the crystal structure has been solved with X-ray diffraction analysis. The crystal is triclinic with the space group of $P\bar{1}$ and cell dimensions of 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)°, V=2547.4 Å^3, and Z=2. The structure have been solved by heavy atom method and the final discrepancy index R_1 was 0.094 and R_2 was 0.090. The cation is structurally identical with those of *cis*-Diammineplatinum α-Pyridone Yellow(PPY), $[Pt_4(NH_3)_8(C_5H_4NO)_4]^{4+}$, *cis*-Diammineplatinum α-Pyridone Blue(PPB), $[Pt_4(NH_3)_8((C_5H_4NO)_4]^{5+}$, and *cis*-Diammineplatinum α-Pyrrolidone Tan(PPT), $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{6+}$, and 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 Pt-Pt bond distances are 2.848(2), 2.875(2), 2.839(2), and 2.875(2) Å, which are intermediate between those of PPY and PPB, indicating that the average platinum oxidation state is between 2.0 and 2.25. According to the potentiometric oxidative titration of the compound using Ce(IV), the average platinum oxidation state is 2.14 and therefore the compound is considered to consist of 44% of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{4+}$ and 56% of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$.

Although a class of dark blue platinum compounds, so called "Platinum Blues," was first reported as early as 1908[1)] and have attracted interest of chemists because of their abnormally deep blue color and paramagnetic nature,[2–4)] their structure and formulas have long been unknown, because they are unstable in solution, difficult to synthesize reproducibly and to obtain crystals.

Recently, Barton *et al.* first reported the synthesis of crystalline *cis*-Diammineplatinum α-Pyridone Blue (PPB), $[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_5\cdot H_2O$, and solved the structure by X-ray analysis.[5,6)] The compound is a tetranuclear chain cation, whose neighboring platinum atoms are bridged by amide oxygen and deprotonated amide nitrogen atoms. Three of the platinum atoms are formally in the oxidation state of +2, and the remaining one is +3; that is, the average platinum 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.[6)]

Following the synthesis and structure determination of PPB, several platinum-blue related compounds have been isolated and structurally elucidated. These include *cis*-Diammineplatinum α-Pyridone Yellow (PPY), $[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_4$,[7)] *cis*-Diammineplatinum 1-Methylhydantoin Yellow (PHY), $[Pt_4(NH_3)_8(C_4H_5N_2O_2)_4](NO_3)_4\cdot H_2O$,[8)] *cis*-Diammineplatinum α-Pyrrolidone Tan (PPT), $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O$,[9,10)] and *cis*-Diammineplatinum α-Pyrrolidone Green (PPG), $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_{5.48}\cdot 3H_2O$.[11)] The last compound is nonstoichiometric, being a mixture of diamagnetic hexavalent PPT cation and paramagnetic PPB-corresponding quinquevalent cation. This nonstoichiometry has been confirmed both with single crystal X-ray diffraction analysis and magnetic susceptibility measurement.[11)] PPT consists of two Pt(II) and two Pt(III) atoms, whose two unpaired electrons are strongly diamagnetically coupled.[10)] PPY and PHY have all their four platinum atoms in the oxidation state of 2+ and are therefore diamagnetic. These compounds reveal that "Platinum Blues" are a class of compounds whose platinum oxidation state can be varied without basic structural change and the color varies according to the platinum oxidation state.

In this paper, another platinum blue related compound, *cis*-Diammineplatinum α-pyrrolidone Violet (PPV), is reported. This compound is nonstoichiometric, being a mixture of PPB-corresponding quinquevalent cation and PPY-corresponding quadrivalent cation. A preliminary report on the structural analysis of the compound has been publlshed previously,[12)] Therefore the details of the crystal structure is reported here, together with the result of the potentiometric oxidative titration using Ce(IV), which confirms the average platinum oxidation state of 2.14.

Experimental

Preparation. The preparation procedure of the compound has been already reported in Ref. 12. The results of the elemental analyses are: Found: C, 10.79; H, 3.32; N, 11.70; Pt, 43.4%. Calcd for $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_2(NO_3)_{2.56}\cdot 5H_2O$: C, 10.72; H, 3.27; N, 11.38; Pt, 43.55%.

Crystal Data. The single crystal of the compound used for intensity measurement was 0.25×0.2×0.1 mm. 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°<2θ<35° measured on a Philips PW1100 diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The crystal data are as follows:

$[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_2(NO_3)_{2.56}\cdot 5H_2O$
triclinic $P\bar{1}$
a = 13.530(8)

$b = 19.242(9)$
$c = 10.222(3)$ Å
$\alpha = 96.56(9)$
$\beta = 93.82(9)$
$\gamma = 74.64(8)^\circ$
$v = 2547.4$ Å^3
MW = 1791.9
$Z = 2$
$D_m = 2.40$
$D_x = 2.34\ \mathrm{g\ cm^{-3}}$
$\mu = 117.4\ \mathrm{cm^{-1}}$ (for Mo $K\alpha$ radiation)

Data Collection. All the intensities within $3^\circ < 2\theta < 55^\circ$ were measured on a Philips PW1100 four-cirle diffractometer. The scan mode was ω—2θ, with a scan rate of 2° min^{-1} in 2θ. The scan range was calculated for each reflection according to the formula, $\omega = 1.2 + 0.3\tan\theta$, and stationary-crystal, stationary-counter background measurement was employed. The background measurement time, T_{bck}, was determined according to the formula, $T_{\mathrm{bck}} = (\mathrm{scan\ time})/2(I_{\mathrm{bck}}/I_{\mathrm{int}})^{1/2}$, where I_{bck} (counts/s) is average value preliminarily measured at both ends and I_{int} (counts/s) is the value of the peak. The measurement was carried out on a crystal sealed in a glass capillary in order to avoid crystal deterioration after long irradiation. Three standard reflections were monitored every two hours, however only random statistical fluctuations were observed throughout the measurement. The data were corrected for the Lorentz-polarization effects and absorption. A total of 8377 reflections with $|F_o| \geq 3\sigma(|F_o|)$ were used for calculation.

Solution and Refinement of the Structure. The coordinates of the four platinum atoms were found from a Patterson map, and a series of block-diagonal least-squares refinements followed by Fourier synthesis revealed all the oxygen, nitrogen, and carbon atoms in the α-pyrrolidonate and ammine ligands. After further refinement of the coordinates with anisotropic temperature factors for all the atoms, a difference synthesis was calculated and all the nitrate and hexafluorophosphate anions and water molecules of crystallization were located. Hydrogen atoms could not be located even with a difference synthesis using the refined coordinates of all the atoms. The structure was finally refined with anisotropic temperature factors for all the atoms to the final discrepancy index of $R_1 = 0.094$ and $R_2 = 0.090$, 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. All the calculations were performed with the local version of

TABLE 1. POSITIONAL AND ISOTROPIC PARAMETERS WITH THEIR STANDARD DEVIATIONS IN PARENTHESES. POSITIONAL PARAMETERS ARE MULTIPLIED BY 10^5 FOR PLATINUM AND BY 10^3 FOR THE OTHER

	X	Y	Z	B_{eq}/Å^2
PT 1	2758 (10)	6696 (7)	3671 (14)	3.0(1)
PT 2	12852 (12)	18015 (7)	9033 (16)	3.5(1)
PT 3	48319 (11)	55246 (6)	40591 (13)	2.9(1)
PT 4	46160 (13)	67446 (7)	26392 (14)	3.6(1)
NH1	−76 (3)	110 (2)	−99 (3)	4.3(4)
NH2	−80 (2)	100 (2)	183 (3)	4.0(3)
NH3	51 (3)	255 (2)	−40 (4)	5.7(4)
NH4	45 (3)	246 (2)	250 (3)	5.1(4)
NH5	533 (3)	473 (2)	249 (3)	4.9(4)
NH6	336 (4)	545 (2)	371 (3)	5.6(4)
NH7	490 (3)	631 (2)	70 (3)	4.9(4)
NH8	319 (3)	704 (2)	221 (3)	5.0(4)
O11	131 (2)	30 (1)	−106 (2)	3.7(3)
N11	216 (2)	121 (2)	−61 (3)	3.7(3)
C11	200 (3)	60 (2)	−121 (3)	3.3(3)
C21	282 (3)	30 (2)	−226 (4)	5.0(4)
C31	353 (6)	82 (4)	−206 (7)	10.2(7)
C41	308 (5)	141 (3)	−97 (6)	7.6(6)
O12	124 (2)	21 (1)	176 (3)	4.4(4)
N12	206 (2)	114 (2)	214 (3)	3.9(4)
C12	189 (3)	50 (2)	236 (4)	4.4(4)
C22	263 (4)	16 (2)	343 (5)	5.2(5)
C32	339 (5)	61 (4)	371 (7)	9.4(7)
C42	291 (4)	131 (3)	292 (6)	6.9(5)
O13	614 (3)	557 (1)	446 (2)	5.5(4)
N13	610 (4)	660 (2)	303 (3)	6.7(5)
C13	664 (3)	603 (2)	376 (4)	4.3(4)
C23	774 (4)	602 (3)	393 (5)	6.0(5)
C33	774 (6)	668 (4)	327 (10)	11.5(7)
C43	670 (5)	694 (3)	262 (7)	7.5(6)
O14	438 (2)	628 (1)	564 (2)	4.1(3)
N14	434 (3)	723 (1)	448 (3)	4.0(3)
C14	432 (3)	697 (2)	561 (4)	4.0(3)
C24	408 (4)	750 (2)	675 (4)	4.8(4)
C34	411 (7)	819 (3)	622 (6)	9.9(7)
C44	423 (6)	804 (2)	472 (4)	8.4(7)
P 1	617 (1)	138 (1)	−40 (1)	4.3(4)
P 2	289 (1)	349 (1)	191 (1)	5.8(4)
F 1	698 (2)	144 (1)	−145 (3)	6.7(6)
F 2	707 (3)	129 (2)	67 (4)	9.8(8)
F 3	542 (3)	134 (2)	65 (3)	7.8(6)
F 4	529 (2)	152 (2)	−147 (4)	9.4(8)
F 5	639 (3)	55 (1)	−76 (4)	10.0(7)
F 6	604 (3)	223 (1)	−1 (3)	8.9(6)
F 7	333 (6)	277 (3)	109 (7)	20.9(11)
F 8	393 (4)	373 (3)	191 (7)	16.1(10)
F 9	337 (5)	318 (3)	328 (4)	15.0(11)
F10	241 (4)	425 (2)	271 (6)	14.8(10)
F11	190 (5)	321 (5)	218 (8)	22.1(13)
F12	251 (6)	378 (3)	67 (5)	19.1(13)
N 1	291 (3)	530 (2)	5 (3)	4.8(4)
N 2	790 (3)	290 (2)	113 (4)	5.6(4)
N 3	12 (5)	826 (3)	425 (5)	4.7(4)
N 4	38 (17)	462 (20)	409 (27)	31.2(14)
O 1	265 (4)	504 (2)	−97 (4)	9.0(8)
O 2	386 (3)	520 (2)	34 (4)	7.3(5)
O 3	233 (4)	563 (2)	84 (4)	9.4(7)
O 4	832 (3)	260 (2)	13 (3)	6.5(6)
O 5	824 (3)	263 (2)	223 (4)	7.5(6)
O 6	704 (3)	337 (2)	110 (3)	7.0(6)
O 7	−56 (8)	840 (6)	344 (10)	11.9(9)
O 8	96 (6)	833 (4)	437 (7)	9.6(8)
O 9	−47 (12)	855 (8)	503 (15)	15.9(13)
O10	115 (12)	497 (7)	410 (10)	13.9(11)
O11	−43 (15)	465 (10)	480 (21)	22.7(12)
O12	23 (17)	459 (17)	286 (26)	39.3(13)
OW 1	−36 (21)	593 (9)	27 (25)	24.4(14)
OW 2	−52 (8)	397 (5)	159 (13)	7.8(7)
OW 3	418 (48)	87 (28)	347 (46)	21.3(9)
OW 4	30 (25)	836 (15)	553 (10)	24.2(11)
OW 5	76 (11)	789 (6)	311 (11)	10.0(8)
OW 6	−4 (13)	−102 (6)	385 (14)	14.3(10)
OW 7	−24 (16)	−206 (15)	444 (16)	18.0(12)
OW 8	−200 (16)	366 (9)	437 (17)	16.1(14)
OW 9	−200 (12)	402 (7)	393 (14)	10.9(9)
OW10	−205 (10)	328 (7)	492 (15)	11.0(10)
OW11	651 (30)	159 (12)	396 (32)	29.9(12)

the program UNICS (Sakurai, 1967) and ORTEP (Johnson, 1965).

The final positional and thermal parameters of non-hydrogen atoms are listed in Table 1. The observed and calculated structure factors and anisotropic temperature factors are avilable at the office of this Bulletin (Document No. 8516).

Oxidative Titration. In order to confirm the average platinum oxidation state, oxidative titration using Ce(IV) was carried out. The titration was monitored potentiometrically by using platinum *vs.* AgCl electrodes. The titrant Ce(IV) was prepared by dissolving ammonium cerium(IV) sulfate in 0.36 mol dm^{-3} sulfuric acid to the concentration of 6.1×10^{-3} mol dm^{-3}. About 0.01 g of *cis*-Diammineplatinum α-Pyrrolidone Violet was weighed and dissolved in 40 ml of 0.1 mol dm^{-3} 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.

Description of the Structure and Discussion

Unit cell has two independent platinum tetranuclear cations. The structure of one of them and the atomic-numbering schemes are depicted in Ref. 12. The interatomic distances and bond angles within the cations are listed in Tables 2 and 3, respectively. 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. Each cation has crystallographic center of symmetry at the midpoint of Pt1-Pt1′ and Pt3-Pt3′ bonds, respectively. These central Pt-Pt bondings are 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 atoms. The structure of the cation is basically identical with those of PPB, PPY, PHY, PPT, and PPG. The Pt-Pt bond distances are closely related to the average platinum oxidation state in the tetranuclear platinum chain compounds[10] as well as in one-dimensional platium complexes.[15] The Pt-Pt bond length of PPV suggests that the compound consists of platinum atoms with intermediate oxidation state between 2.0 and 2.25.[12] The compound contains 2.56 nitrate anions per cation as concluded later in the discussion of the oxidative titration using Ce(IV). From the X-ray diffraction analysis, two nitrate anions (N1 and N2) have been located with statistical weight of unity, and another two (N3 and N4), with statistical weight of less than unity. The latter two are considered to be distributed in the crystal lattice with a weight of 0.56/2. However, no definite conclusion can be drawn concerning the platinum oxidation state, simply from the number of nitrate anions found in the crystal lattice. The average platinum oxidation state has been confirmed by oxidative titration and the detail is described later in this paper.

Table 2. Interatomic distances (l/Å) within the cations with their estimated standard deviations in parentheses

Coordination Spheres			
Pt1-Pt2	2.848(2)	Pt3-Pt4	2.839(2)
Pt1-Pt1′	2.875(2)	Pt3-Pt3′	2.875(2)
Pt1-NH1	1.99(3)	Pt3-NH5	2.10(2)
Pt1-NH2	2.09(3)	Pt3-NH6	2.04(4)
Pt1-O11	2.02(2)	Pt3-O13	1.82(5)
Pt1-O12	1.98(2)	Pt3-O14	2.06(2)
Pt2-NH3	2.10(3)	Pt4-NH7	2.08(2)
Pt2-NH4	2.13(3)	Pt4-NH8	1.90(4)
Pt2-N11	2.05(2)	Pt4-N13	1.98(5)
Pt2-N12	1.96(3)	Pt4-N14	2.01(2)
Pt2-F11	3.15(8)		

Pyrrolidone Rings			
O11-C11	1.26(4)	O13-C13	1.51(5)
C11-C21	1.54(5)	C13-C23	1.49(6)
C21-C31	1.56(10)	C23-C33	1.52(10)
C31-C41	1.53(8)	C33-C43	1.50(9)
N11-C41	1.49(7)	N13-C43	1.28(8)
O12-C12	1.26(5)	O14-C14	1.30(4)
C12-C22	1.52(5)	C14-C24	1.46(4)
C22-C32	1.51(9)	C24-C34	1.51(7)
C32-C42	1.62(9)	C34-C44	1.53(7)
N12-C42	1.44(6)	N14-C44	1.52(4)

Table 3. Interatomic bond angles (ϕ/°) in the cations with their estimated standard deviations in parentheses

Coordination Spheres			
Pt2-Pt1-Pt1′	166.53(6)	Pt4-Pt3-Pt3′	168.31(6)
NH1-Pt1-NH2	91.3(13)	NH5-Pt3-NH6	90.6(16)
NH1-Pt1-N11	96.7(11)	NH5-Pt3-O13	90.8(15)
NH1-Pt1-N12	136.6(11)	NH5-Pt3-O14	178.0(9)
NH2-Pt1-N11	137.3(11)	NH6-Pt3-O13	176.5(19)
NH2-Pt1-N12	94.6(11)	NH6-Pt3-O14	90.3(15)
N11-Pt1-N12	52.5(9)	O13-Pt3-O14	88.2(14)
NH3-Pt2-NH4	90.0(14)	NH7-Pt4-NH8	90.3(15)
NH3-Pt2-O11	89.1(11)	NH7-Pt4-N13	90.5(17)
NH3-Pt2-O12	139.2(11)	NH7-Pt4-N14	176.4(11)
NH4-Pt2-O11	139.7(10)	NH8-Pt4-N13	170.6(20)
NH4-Pt2-O12	97.8(10)	NH8-Pt4-N14	89.1(15)
O11-Pt2-O12	52.1(6)	N13-Pt4-N14	89.5(17)

Pyrrolidone Rings			
Pt2-N11-C11	123 (2)	Pt4-N13-C13	120 (3)
Pt2-N11-C41	120 (3)	Pt4-N13-C43	128 (3)
Pt1-O11-C11	122 (2)	Pt3-O13-C13	122 (2)
N11-C11-O11	129 (3)	N13-C13-O13	124 (3)
N11-C11-C21	109 (3)	N13-C13-C23	111 (4)
O11-C11-C21	122 (3)	O13-C13-C23	124 (3)
C11-C21-C31	104 (4)	C13-C23-C33	100 (4)
C21-C31-C41	107 (5)	C23-C33-C43	108 (6)
C31-C41-N11	103 (4)	C33-C43-N13	108 (5)
Pt2-N12-C12	126 (2)	Pt4-N14-C14	132 (2)
Pt2-N12-C42	119 (3)	Pt4-N14-C44	118 (2)
Pt1-O12-C12	123 (2)	Pt3-O14-C14	122 (2)
N12-C12-O12	127 (3)	N14-C14-O14	121 (3)
N12-C12-C22	111 (3)	N14-C14-C24	116 (3)
O12-C12-C22	123 (3)	O14-C14-C24	123 (3)
C12-C22-C32	106 (4)	C14-C24-C34	103 (3)
C22-C32-C42	104 (4)	C24-C34-C44	108 (3)
C32-C42-N12	104 (4)	C34-C44-N14	103 (3)

TABLE 4. CHARACTERISTIC BOND LENGTHS IN COORDINAITON SPHERES OF PLATINUM TETRANUCLEAR COMPOUNDS

Compound	Av Pt oxdn state	Distance (l/Å) Pt-Pt	Pt-L$_{axial}$	Ref
$[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_4$ α-pyridone (PPY)	2.0	2.88[a] 3.13[b]		7
$[Pt_4(NH_3)_8(C_4H_5N_2O_2)_4](NO_3)_4 \cdot H_2O$ 1-methylhydantoin (PHY)	2.0	3.131[a] 3.204[b]		8
$[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_2(NO_3)_{2.56} \cdot 5H_2O$ α-Pyrrolidone (PPV)	2.14	2.848[a] 2.839[a] 2.875[b] 2.875[b]	3.15 (PF_6^-)	this work
$[Pt_4(NH_3)_8(C_5H_4NO)_4](NO_3)_5 \cdot H_2O$ α-Pyridone (PPB)	2.25	2.7745[a] 2.8770[b]	3.32 (NO_3^-)	6
$[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_{5.48} \cdot 3H_2O$ α-Pyrrolidone (PPG)	2.37	2.764[a] 2.761[a] 2.739[b] 2.724[b] 2.740[a] 2.753[a]	3.21 (NO_3^-) 2.95 (NO_3^-)	11
$[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ α-Pyrrolidone (PPT)	2.5	2.70[a] 2.71[b] 2.70[a]	2.60 (NO_3^-) 2.72 (NO_3^-)	10

a) Bond length related to terminal Pt-Pt bond. b) Bond length related to central Pt-Pt bond.

TABLE 5. CHARACTERISTIC BOND ANGLES IN PLATINUM TETRANUCLEAR COMPOUNDS

Compound	Dihedral angle,[c] deg		Pt-Pt-Pt Angle, deg	Ref
	τ	ω		
PPY	30.0[a]	21	158.40	7
PHY			160.5	8
PPV	26.2[a] 23.2[a]	0.9 3.2 1.1 4.5	166.53 168.31	This work
PPB	27.4[a]	21.7 23.9	164.60	6
PPG	24.5[a] 26.9[a] 17.4[b] 15.9[b]	0.8 0.8 16.8 1.2 12.8 0.2 3.8 7.0	166.6 168.5 167.2 170.9	11
PPT	18.7[a] 21.2[b]	4.1 4.5 5.0 5.1	170.4 168.8	10

a) Bond angle related to terminal Pt-Pt bond. b) Bond angle related to central Pt-Pt bond. c) τ is the tilt angle betewen adjacent platinum coordination planes and ω is the torsion (or twist) angle about the Pt-Pt vector.

Tables 4 and 5 summarizes the geometric features of PPY, PPV, PPB, PPG, and PPT. In PPY, PPV, 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. Comparing the difference of the terminal and central Pt-Pt bond lengths in these tetranuclear cations, it seems that the difference of the bond lengths between terminal and central Pt-Pt bonds is specific to the bridging amide ligand and the difference is larger in α-pyridone compounds than α-pyrrolidone ones. The difference is also dependent on the platinum oxidation state and, as the average oxidation state is increased, the difference seems to be decreased. Comparing PPV, PPG, and PPT, the tilt sngle 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 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. Concerning the torsion angles ω about the Pt-Pt vector, there seems to be a distinct difference between α-pyridone compounds and α-pyrrolidone ones. While in PPY and PPB, where the amide ligand is α-pyridone, the angles are about 22°, most of them are decreased to less than 6° in PPG, PPT, and PPV containing α-pyrrolidone. The reason for the remarkably different two ω angles larger than 10° in PPG still remains unexplained even with the present structural analysis of PPV. The small ω values less than 6° signify that the bridging N(ring) and O(exocyclic) in the α-pyrrolidone are almost overlapped when viewed along the Pt-Pt vector for α-pyrrolidone compounds, PPV, PPG, and PPT, while in α-pyridone compounds, PPY and PPB, ω values are about 22°, which suggest that N(ring) and O(exocyclic) are twisted about the Pt-Pt vector. Apart from these tetranuclear compounds, there are several amidate-bridged Pt(II) dimers whose structures have been studied by X-ray diffraction analyses. These include $[Pt_2(NH_3)_4(C_5H_4NO)_2](NO_3)_2 \cdot 2H_2O$ (α-pyridone dimer),[16] $[Pt_2(NH_3)_4(C_6H_7N_2O_2)_2]$ $(NO_3)_2 \cdot H_2O$ (1-methylthymine dimer),[17] $[Pt_2(NH_3)_4(C_5H_5N_2O_2)_2]$-

$(NO_3)_2\cdot 3H_2O$ (1-methyluracil dimer,[18]) $[Pt_2(NH_3)_4(C_5H_6N_3O)_2]\text{-}(NO_3)_2\cdot 2H_2O$ (1-methylcytosine dimer).[20]) The torsion angles ω in these dimers are all within the range of 13° to 20°, except in 1-methylthymine dimer, where ω is 1.0°. It seems, therefore, the torsion angle is specific to each amide ligand and the effect of platinum oxidation state on ω value is less, compared with that of an amide ligand.

No significant difference was observed in Pt–O, Pt–N, and Pt–NH_3 bond lengths among the six tetranuclear platinum compounds and these values are within the range normally observed in related platinu-(II) ammine complexes.[16–28]) The coordination sphere of each platinum atom is almost planar. The shifts of each platinum atom from the least-squares planes are Pt1 0.05 Å, Pt2 0.06 Å, Pt3 0.04 Å, and Pt4 0.02 Å. The average P–F distance in PF_6^- anions is 1.57 Å with the standard deviation of 0.04 Å. All the N–O distances and bond angles within the nitrate anions are within the usual values (average N–O distance, 1.24 Å).

TABLE 6. POSSIBLE HYDROGEN BONDING (Å) IN THE CRYSTAL LATTICE[a])

NH1···OW6 (i)	3.15(16)	O4···NH8(v)	3.09(4)
NH5···O10(ii)	3.03(13)	NH2···OW4(vi)	2.94(17)
O13···NH6(ii)	2.87(4)	OW8···O14(vi)	3.18(21)
O5···NH2(iii)	3.05(4)	NH4···OW4(vi)	3.08(27)
O5···OW9(iii)	2.97(13)	NH6···OW10(vi)	3.01(12)
O4···NH1(iii)	2.96(3)	O14···OW10(vi)	3.07(12)
NH4···O5(iv)	2.92(5)	NH6···OW8(vi)	3.02(17)
NH1···O4(iv)	2.96(3)	O14···OW8(vi)	3.18(21)
NH3···O4(iv)	3.01(5)	NH1···OW5(vii)	3.07(13)
NH7···O6(v)	3.07(5)	OW1···NH3(vii)	2.86(18)
NH8···O4(v)	3.09(4)	O1···OW2(vii)	3.08(10)
NH7···O2(v)	3.05(4)		

a) Roman numerals refer to the symmetry translations as follows: i(−*x*, −*y*, −*z*), ii(1−*x*, 1−*y*, 1−*z*), iii(1+*x*, *y*, *z*), iv(−1+*x*, *y*, *z*), v(1−*x*, 1−*y*, −*z*), vi(−*x*, 1−*y*, 1−*z*), vii(−*x*, 1−*y*, −*z*).

Table 6 summarizes the possible hydrogen bondings in the crystal lattice. The crystal packing is shown in Fig. 1. 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 amidatebridged dinuclear and tetranuclear compounds of platinum(II) and platinum(III).[29]) In the present compound, only one loose coordination, Pt2–F11 3.15(8) Å, is found as shown in Table 2, and no other significant coordination to platinum atoms at chain ends are observed within 3.5-Å range. This is probably due to the low average platinum oxidationstate of the compound. The bond length 3.15 Å of Pt2–F11 is slightly shorter than the axial bond length of 3.32 Å for Pt–O(NO_3^-) found in PPB, even if we take into consideration the difference of the ionic radii of O^{2-} (1.40 Å) and F^- (1.33 Å). It is rather comparable to 3.21 Å of Pt–O(NO_3^-) found in PPG. The axial bond length would therefore be determined firstly by average platinum oxidation state, however it is also affected by other forces probably imposed by the crystal packing.

The results of the potentiometric oxidative titration with Ce(IV) in 0.29 mol dm^{-3} and 0.93 mol dm^{-3} HNO_3 are shown in Fig. 2. Both results show that the average platinum oxidation state is 2.14, however, the titration curve is different. While in 0.29 mol dm^{-3} HNO_3 the compound is directly oxidized to Pt(III) state, in 0.93 mol dm^{-3} HNO_3, it is first oxidized to $Pt^{2.5+}$ and secondly to Pt(III), as shown in Fig. 2. From the relation curve

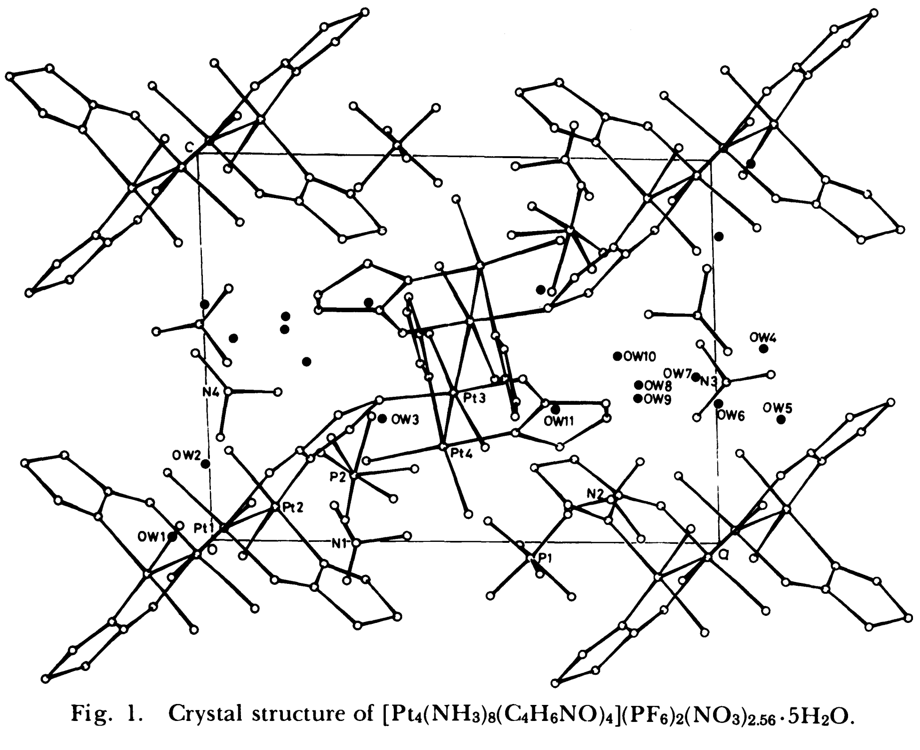

Fig. 1. Crystal structure of $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_2(NO_3)_{2.56}\cdot 5H_2O$.

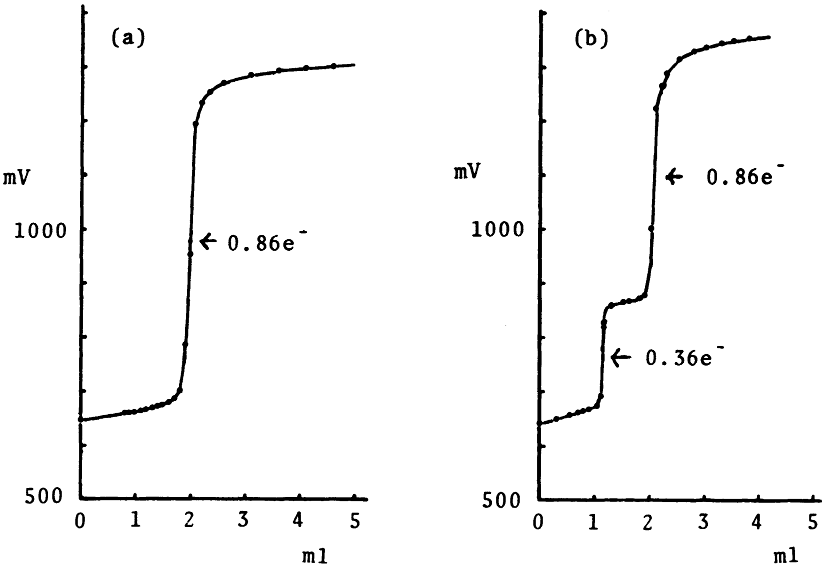

Fig. 2. Potentiometric oxidative titration of PPV with Ce(IV); (a) 0.29 mol dm^{-3} HNO_3 solution, (b) 0.93 mol dm^{-3} HNO_3 solution.
The titrations were monitored by using platinum *vs.* AgCl electrodes.

of Pt–Pt bond distance and average platinum oxidation state,[11] the average platinum oxidation state in the present compound is 2.10 (from the terminal Pt–Pt bond lengths) or 2.25 (from the central Pt–Pt bond lengths). Since the relation still seems to require more data to be recognized as established, we currently adopt the result of oxidative titration and determine the average platinum oxidation state as 2.14. This means that the compound is $[Pt_4(NH_3)_8(C_4H_6NO)_4](PF_6)_2(NO_3)_{2.56}\cdot 5H_2O$, being a mixture of 44% of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{4+}$ and 56% of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{5+}$. The fact that the existence ratio of the two cations is nearly 1:1 does not seem to mean any particular inter-cationic or intercation and -anion interactions, since there seems no significant interacions between them in the crystal pscking. Therefore it seems probable that other crystals with different existence ratio exist. Such possibility is now under investigation.

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