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Preparation and Structural Characterization of Two Mixed NH_3/Cl/1-Methylthymine Diplatinum(II) Complexes: *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)Cl][Pt(NH_3)Cl_3]\cdot H_2O$ and *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2PtCl_2\cdot 3H_2O$

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Received June 28, 1989

Compounds obtained through reaction of *cis*-$A_2Pt(1\text{-}MeT)_2$ (1-MeT = 1-methylthymine anion, $C_6H_7N_2O_2$; A = NH_3 or A_2 = bpy) and *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2]^{2+}$ (head-head) with the Pt-containing anions $[Pt(NH_3)Cl_3]^-$ and $[PtCl_4]^{2-}$ as well as $[PdCl_4]^{2-}$ have been isolated and characterized. Two examples have been studied by X-ray analysis, *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)Cl][Pt(NH_3)Cl_3]\cdot H_2O$ (**1**) and *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2PtCl_2\cdot 3H_2O$ (**2**). These two new compounds complete a series of three closely related dinuclear Pt complexes of +2, +1, and 0 charge, containing two bridging 1-MeT ligands in the head-head arrangement. **1** crystallizes in the orthorhombic system, space group *Pbca*, with $a = 27.801$ (3) Å, $b = 13.049$ (2) Å, $c = 14.110$ (2) Å, $V = 5118.8$ Å^3, and $Z = 8$. **2** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 11.185$ (3) Å, $b = 10.606$ (3) Å, $c = 9.808$ (3) Å, $\alpha = 110.44$ (2)°, $\beta = 95.21$ (2)°, $\gamma = 99.00$ (2)°, $V = 1073.0$ Å^3, and $Z = 2$. In both compounds Pt binding is through N3 and O4. Pt-Pt separations within the dinuclear units are 2.939 (1) Å (**1**) and 2.861 (1) Å (**2**), and the Pt planes are nearly eclipsed, torsional angles being 0.8° (**1**) and 3.0° (**2**). Neither $[Pt(NH_3)Cl_3]^-$ nor $[PtCl_4]^{2-}$ coordinates to the head-head dinuclear $[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2](NO_3)_2$ but rather undergoes anion exchange with nitrate.

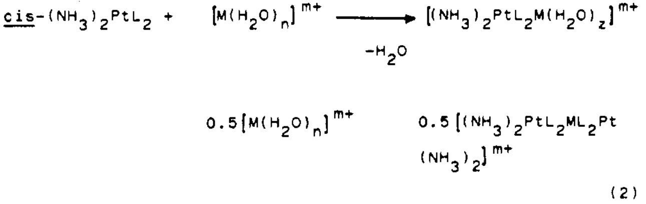
Introduction

The systematic study of polynuclear complexes of *cis*-$(NH_3)_2Pt^{II}$ with uracil and thymine nucleobases is of interest for several reasons, e.g. (i) the elucidation of structural features of "platinum pyrimidine blues", a class of interesting antitumor agents,[2] (ii) the question of Pt oxidation state and its stabilization[3] in these compounds and in related heteronuclear systems, and (iii) the aspect of interaction between Pt and heterometals at close distance.[4]

Up to now, we have been primarily concerned with cationic complexes that we considered likely building blocks of the "blues" or models thereof. These complexes were prepared either through condensation reactions between mononuclear complexes,[5] e.g. according to

$$2[(NH_3)_2Pt(H_2O)L]^+ \rightarrow [(NH_3)_2PtL_2Pt(NH_3)_2]^{2+} + 2H_2O \qquad (1)$$

(L = 1-methyluracil anion, 1-MeU, or 1-methylthymine anion, 1-MeT), or via condensation of a neutral *cis*-$(NH_3)_2PtL_2$ species with cations such as $[A_2M(H_2O)_2]^{2+}$ (A = NH_3[6] or A_2 = en, bpy;[7] M = Pt, Pd[7,8]) and $[M'(H_2O)_n]^{m+}$.[9,10]



$$\begin{array}{lll} & [A_2M(H_2O)_2]^{m+} & [(NH_3)_2PtL_2MA_2]^{m+} \\ \underline{cis}\text{-}(NH_3)_2PtL_2 \; + & [M(H_2O)_n]^{m+} \xrightarrow[-H_2O]{} & [(NH_3)_2PtL_2M(H_2O)_z]^{m+} \\ & 0.5[M(H_2O)_n]^{m+} & 0.5[(NH_3)_2PtL_2ML_2Pt(NH_3)_2]^{m+} \end{array} \qquad (2)$$

While the first route (eq 1) gives dinuclear complexes with head-tail-arranged L ligands, the latter leads to di- and trinuclear complexes with pairs of L arranged head-head. Dinuclear PtPt complexes may form larger aggregates through coordination of additional cations[5,11,12] and through partial oxidation and formation of an intermolecular Pt-Pt bond, respectively.[13]

In this paper, we report, among others, on two dinuclear complexes, *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)Cl][Pt(NH_3)Cl_3]$ and *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2PtCl_2$, obtained from *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2$ and the anions $[Pt(NH_3)Cl_3]^-$ and $[PtCl_4]^{2-}$, respectively. The two new compounds complete a series of three related dinuclear complexes of +2, +1 and 0 charge, containing bridging 1-MeT ligands in the head-head arrangement.

Experimental Section

Preparations. *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2(aq)$,[6] *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2](NO_3)_2$,[6] and $(bpy)Pt(1\text{-}MeT)_2\cdot 4H_2O$[7] were prepared as previously described. $K[(NH_3)PtCl_3]$ was obtained from $NH_4[(NH_3)PtCl_3]$[14] via cation exchange.

***cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)Cl][Pt(NH_3)Cl_3]\cdot H_2O$ (1).** *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2\cdot 2.5H_2O$ (1 mmol) was dissolved in N_2-saturated water (30 mL), and $K[Pt(NH_3)Cl_3]$ (2 mmol), dissolved in N_2-saturated water (5 mL), was added. The yellow mixture was kept in a stoppered flask at 4 °C. After 5 days, yellow-green crystals were harvested, which proved suitable for X-ray analysis. After 2 more weeks, during which the solution became green, a second crop of **1** was obtained. The total yield was 80%. It was found that the quality of the crystals generally was better when $(NH_3)_2Pt(1\text{-}MeT)_2$ was used in excess. Anal. Found (calcd) for **1** ($C_{12}H_{28}N_8O_5Pt_3Cl_4$): C, 13.20 (13.42); H, 2.65 (2.58); N, 10.36 (10.27).

***cis*-$(NH_3)_2Pt(1\text{-}MeT)_2PtCl_2\cdot 3H_2O$ (2).** *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2\cdot 2.5H_2O$ (1 mmol) was dissolved in water (25 mL), and K_2PtCl_4 (1 mmol), dissolved in water (20 mL), was added (pH 4.8). Within 2 days at 22 °C (open beaker), 450 mg of reddish black crystals of **2** had formed, which were filtered out, washed with a small amount of water, and dried in air. On concentration of the filtrate, an additional 60 mg of **2** was obtained. Anal. Found (calcd) for **2** ($C_{12}H_{26}N_6O_7Pt_2Cl_2$): C,

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Table I. Crystallographic Data for **1** and **2**

	1	**2**
formula	$C_{12}H_{28}N_8O_5Pt_3Cl_4$	$C_{12}H_{26}N_6O_7Pt_2Cl_2$
fw	1091.48	827.52
space group	*Pbca*	$P\bar{1}$
a, Å	27.801 (3)	11.285 (3)
b, Å	13.049 (2)	10.606 (3)
c, Å	14.110 (2)	9.808 (3)
α, deg		110.44 (2)
β, deg		95.21 (2)
γ, deg		99.00 (2)
V, $Å^3$	5118.8	1073.0
Z	8	2
d_{calcd}, g cm^{-3}	2.832	2.56
d_{measd}, g cm^{-3}	2.78[a]	2.59
cryst size, mm	0.1, 0.1, 0.05	0.1, 0.2, 0.3
μ, cm^{-1}	162	127
θ_{range}, deg	2–25	2–25
no. of unique reflcns	4510	3780
no. of reflcns in the calcns	4018 ($F_o > 2\sigma(F_o)$)	3537 ($F_o > 2\sigma(F_o)$)
no. of params	164	262
R	0.074	0.048
$R_w(F)$	0.073[b]	0.049[c]

[a] Sample possibly dehydrated; cf. d_{calcd} for anhydrous compound is 2.786. [b] $w^{-1} = \sigma^2(F) + 0.0012F^2$. [c] $w^{-1} = \sigma^2(F) + 0.0008F^2$.

17.74 (17.42); H, 2.87 (3.17); N, 10.39 (10.16); Cl, 8.27 (8.57). The color of crystalline **2** proved quite variable, ranging from light red to purple and almost black. It appears that the purity of K_2PtCl_4 is responsible for this variety and that impurities of Pt(IV) are responsible for the dark colors. Pure **2** is red.

(bpy)Pt(1-MeT)$_2$PtCl$_2$·3H$_2$O (3) was prepared in analogy to **2**, but the mixture was briefly heated to 60 °C to dissolve (bpy)Pt(1-MeT)$_2$. A dark red precipitate (21% yield) of **3** was filtered out, washed with water and acetone, and dried in air. Anal. Found (calcd) for **3** ($C_{22}H_{28}N_6O_7Cl_2Pt_2$): C, 27.73 (27.83); H of dehydrated sample, 2.27 (2.34); N, 8.74 (8.85); Cl, 7.87 (7.47).

(bpy)Pt(1-MeT)$_2$PdCl$_2$·2H$_2$O (4) was obtained in 74% yield by adding K_2PdCl_4 to a suspension of (bpy)Pt(1-MeT)$_2$ in water. The tan precipitate that formed was filtered out, washed with water, acetone, and ether, and dried in air. Anal. Found (calcd) for **4** ($C_{22}H_{26}N_6O_6Cl_2PtPd$): C, 31.38 (31.35); H, 2.57 (2.75); N, 9.88 (9.97); Cl, 8.89 (8.41).

[(NH$_3$)$_2$Pt(1-MeT)$_2$Pt(NH$_3$)$_2$][PtCl$_4$] (5) precipitated as colorless microcrystals by mixing a warmed solution of *cis*-[(NH$_3$)$_2$Pt(1-MeT)$_2$Pt(NH$_3$)$_2$](NO$_3$)$_2$ (head–head) (0.15 mmol in 10 mL of water) with a solution of K_2PtCl_4 (0.15 mmol in 2 mL of water). The yield was 90%. Anal. (calcd) for **5** ($C_{12}H_{24}N_8O_4Cl_4Pt_3$): C, 13.0 (13.43); H, 2.3 (2.44); N, 10.1 (10.34).

[(NH$_3$)$_2$Pt(1-MeT)$_2$Pt(NH$_3$)$_2$][Pt(NH$_3$)Cl$_3$]$_2$ (6) was obtained as bright yellow columns from a solution of *cis*-[(NH$_3$)$_2$Pt(1-MeT)$_2$Pt(NH$_3$)$_2$](NO$_3$)$_2$ (head–head) (0.05 mmol in 3 mL of water) to which K[(NH$_3$)PtCl$_3$] (0.1 mmol in 1 mL of water) had been added. Crystals isolated after 5 min (35 mg) were washed with a small amount of water and dried in air. Anal. Found (calcd) for **6** ($C_{10}H_{28}N_{10}O_4Cl_6Pt_4$): C, 9.27 (8.93); H, 2.14 (2.10); N, 10.44 (10.41).

Spectroscopy. IR spectra were recorded on Perkin-Elmer 783 and a 580 B spectrometers, and ^1H NMR spectra were recorded on the following instruments: Varian EM 360 A; Bruker WM 250 and AM 300. NMR samples were measured as D_2O solutions ($[NMe_4]^+$ as internal standard, referenced to sodium 3-(trimethylsilyl)propanesulfonate). UV–vis spectra were recorded on Perkin-Elmer 555 and Lambda 12 spectrometers. pH values were measured by use of a glass electrode (Metrohm); for D_2O solutions, 0.4 unit was added to the meter reading.

Table II. Positional Parameters and Temperature factors ($Å^2$) for **1**

atom	*x*	*y*	*z*	*U*
Pt1	0.1259 (1)	0.1936 (1)	1.0721 (1)	0.023 (1)
Pt2	0.1325 (1)	0.2337 (1)	0.8676 (1)	0.029 (1)
N10	0.1943 (6)	0.2316 (12)	1.1132 (12)	0.033 (4)
N11	0.1001 (7)	0.3292 (13)	1.1268 (12)	0.038 (4)
Cl20	0.2111 (2)	0.2806 (5)	0.8534 (4)	0.051 (2)
N20	0.1088 (7)	0.3811 (13)	0.8458 (13)	0.037 (4)
N1a	0.1741 (6)	−0.1132 (11)	1.0809 (11)	0.026 (3)
C1a′	0.1828 (8)	−0.1849 (15)	1.1578 (15)	0.036 (5)
C2a	0.1623 (8)	−0.0155 (15)	1.1074 (14)	0.031 (4)
O2a′	0.1612 (6)	0.0139 (10)	1.1864 (10)	0.038 (3)
N3a	0.1514 (6)	0.0533 (11)	1.0306 (10)	0.024 (3)
C4a	0.1589 (8)	0.0238 (15)	0.9402 (15)	0.032 (4)
O4a′	0.1521 (6)	0.0855 (10)	0.8703 (10)	0.038 (3)
C5a	0.1742 (8)	−0.0766 (15)	0.9183 (14)	0.030 (4)
C5a′	0.1814 (8)	−0.1096 (15)	0.8134 (15)	0.035 (5)
C6a	0.1810 (8)	−0.1412 (15)	0.9881 (14)	0.030 (4)
N1b	−0.0192 (7)	0.1137 (13)	1.0963 (13)	0.038 (4)
C1b′	−0.0516 (11)	0.0855 (20)	1.1768 (19)	0.059 (7)
C2b	0.0286 (9)	0.1333 (17)	1.1140 (16)	0.042 (5)
O2b′	0.0437 (7)	0.1308 (13)	1.1928 (13)	0.061 (5)
N3b	0.0565 (6)	0.1578 (11)	1.0375 (11)	0.026 (3)
C4b	0.0384 (7)	0.1636 (13)	0.9460 (12)	0.021 (3)
O4b′	0.0624 (6)	0.1877 (11)	0.8733 (10)	0.039 (3)
C5b	−0.0114 (8)	0.1423 (15)	0.9327 (15)	0.033 (4)
C5b′	−0.0329 (12)	0.1508 (22)	0.8322 (21)	0.066 (8)
C6b	−0.0395 (9)	0.1201 (17)	1.0043 (16)	0.043 (5)
Pt3	0.3395 (1)	0.0734 (1)	0.9808 (1)	0.030 (1)
Cl30	0.2857 (2)	−0.0039 (5)	1.0809 (4)	0.053 (2)
Cl31	0.3952 (2)	0.0917 (4)	1.0996 (4)	0.048 (2)
Cl32	0.3902 (2)	0.1518 (5)	0.8758 (4)	0.052 (2)
N30	0.2893 (8)	0.0534 (14)	0.8723 (13)	0.045 (5)
O10	0.5044 (13)	0.3865 (27)	0.4658 (22)	0.145 (12)

Table III. Positional Parameters and Temperature factors ($Å^2$) for **2**

atom	*x*	*y*	*z*	*U*
Pt1	0.3574 (1)	0.1191 (1)	0.0872 (1)	0.022 (1)
Pt2	0.1896 (1)	0.2787 (1)	0.0328 (1)	0.031 (1)
Cl1	0.2603 (3)	0.3315 (3)	−0.1542 (4)	0.055 (1)
Cl2	0.0335 (3)	0.1161 (3)	−0.1265 (4)	0.059 (1)
N10	0.4489 (7)	0.1249 (8)	−0.0840 (10)	0.026 (3)
N11	0.2455 (8)	−0.0654 (10)	−0.0409 (11)	0.038 (3)
N1a	0.6467 (7)	0.4255 (9)	0.3724 (11)	0.033 (3)
C1a′	0.7675 (10)	0.4255 (14)	0.4440 (18)	0.052 (6)
C2a	0.5772 (8)	0.3031 (10)	0.2817 (11)	0.026 (3)
O2a′	0.6125 (7)	0.1973 (7)	0.2593 (9)	0.038 (3)
N3a	0.4624 (7)	0.3038 (8)	0.2155 (10)	0.027 (3)
C4a	0.4253 (9)	0.4273 (11)	0.2380 (12)	0.028 (4)
O4a′	0.3230 (6)	0.4308 (7)	0.1765 (9)	0.037 (3)
C5a	0.5015 (9)	0.5545 (10)	0.3311 (12)	0.029 (4)
C5a′	0.4618 (11)	0.6874 (11)	0.3520 (16)	0.044 (5)
C6a	0.6112 (9)	0.5498 (11)	0.3946 (14)	0.034 (4)
N1b	0.2500 (7)	0.0465 (9)	0.4574 (10)	0.032 (3)
C1b′	0.2932 (11)	−0.0307 (13)	0.5424 (15)	0.042 (5)
C2b	0.3040 (9)	0.0447 (11)	0.3370 (12)	0.030 (4)
O2b′	0.3855 (8)	−0.0197 (9)	0.3056 (10)	0.048 (4)
N3b	0.2665 (7)	0.1164 (8)	0.2553 (9)	0.022 (2)
C4b	0.1693 (9)	0.1762 (10)	0.2822 (12)	0.029 (4)
O4b′	0.1273 (6)	0.2435 (8)	0.2043 (9)	0.036 (3)
C5b	0.1093 (9)	0.1719 (11)	0.4046 (13)	0.029 (4)
C5b′	−0.0015 (10)	0.2392 (13)	0.4366 (15)	0.043 (5)
C6b	0.1517 (9)	0.1101 (11)	0.4878 (13)	0.032 (4)
O10	0.2957 (13)	0.6658 (12)	1.0007 (15)	0.089 (6)
O11	0.0317 (14)	0.5536 (15)	0.8001 (19)	0.113 (9)
O12	0.1228 (16)	0.6807 (21)	0.2133 (22)	0.150 (13)

X-ray Crystallography. Single-crystal X-ray diffraction experiments were performed on a Philips PW-1100 diffractometer with Mo Kα radiation (λ = 0.710 69 Å) at ambient temperature. Details of data collection and structure determination are summarized in Table I. Lp effects and in a later stage an empirical absorption[15] correction were applied. Both structures were solved by Patterson methods and refined with the programs of SHELX-76.[16] Hydrogens were ignored. Non-hydrogen atoms were refined anisotropically in the case of **2**. With **1**, only Pt and Cl atoms were refined anisotropically. The anisotropic thermal parameters are included in the supplementary material. Final atomic coordinates are given in Table II (**1**) and Table III (**2**). The highest peaks in the final difference maps were 2.6 e $Å^{-3}$ (0.9 Å away from Pt1) for **1** and 2.0 e $Å^{-3}$ (1.5 Å away from Pt2) for **2**. Complex scattering factors for neutral atoms were taken from ref 17.

Results and Discussion

General Considerations. For the reaction of *cis*-(NH$_3$)$_2$Pt(1-MeT)$_2$ with $[Pt(NH_3)Cl_3]^-$ we anticipated formation of two

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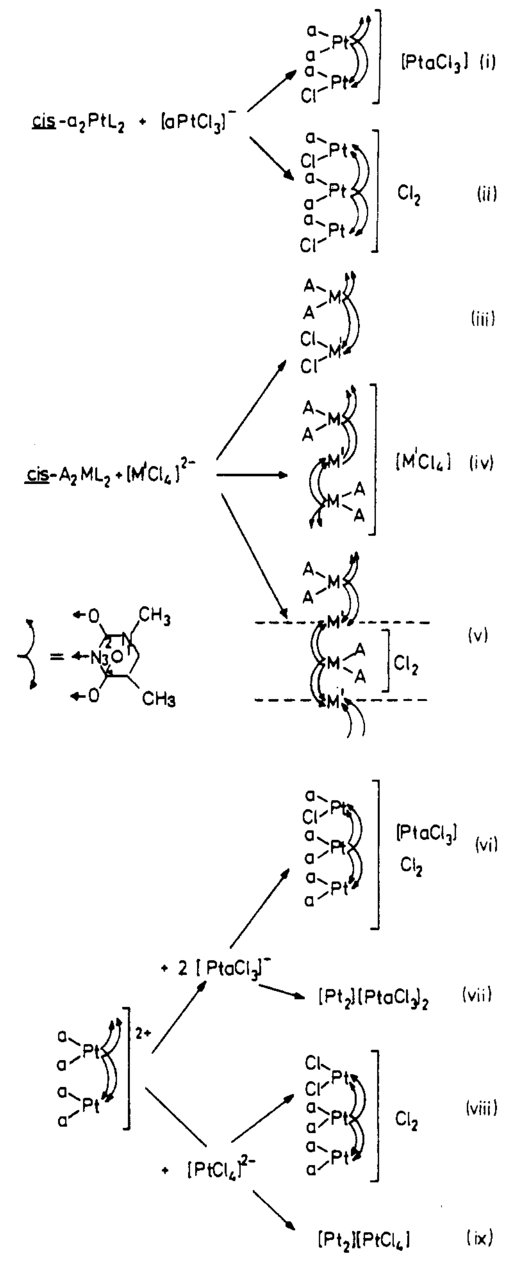
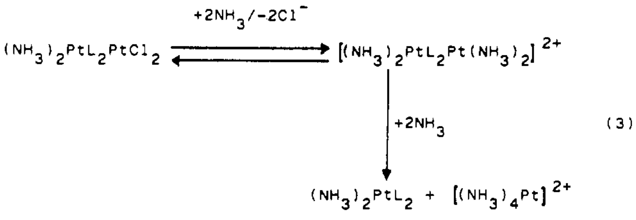


Figure 1. Scheme of possible reaction products of *cis*-$(A)_2Pt(1\text{-}MeT)_2$ and $[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2]^{2+}$ with $[Pt(NH_3)Cl_3]^-$ and $[MCl_4]^{2-}$, respectively.

possible products (Figure 1), a dinuclear complex (i) and a trinuclear one (ii). On the basis of elemental analysis data, a differentiation was not possible, although the close similarity of the IR spectra of **1**, **2**, and $[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2](NO_3)_2$ in general (cf. supplementary material) tentatively favored structure i.

Reactions of *cis*-$A_2M(1\text{-}MeT)_2$ (M = Pt(II), Pd(II)) with $[M'Cl_4]^{2-}$ (M' = Pt(II), Pd(II)) gave compounds of composition $A_2M(1\text{-}MeT)_2M'Cl_2$, for which several feasible structures exist (Figure 1), e.g. of dinuclear (iii), trinuclear (iv) or polynuclear (v) composition. The possibilities are based on established structural features of di- and oligonuclear complexes derived from *cis*-$(NH_3)_2PtL_2$ (L = 1-MeT, 1-MeU) and do not include additional alternatives such as single bridge formation between two metal centers, hydrolysis of Cl ligands, and possible metal exchange processes between Pt and Pd, for example. Moreover, a differentiation between the possibilities of pairwise (e.g. O4,O4) or mixed (e.g. O4,O2)[18] coordination of the exocyclic oxygens on metal binding is not made. Prior to verification in a crystal structure analysis, the dinuclear structure iii was favored for **2** for the following reasons: First, the IR spectrum of **2** was remarkably similar to and over a wide range virtually superimposable with that of the head–head dimer *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2]^{2+}$ as far as 1-MeT modes were concerned. In particular, the double-bond stretching region of both compounds (e.g. very strong bands at 1660 and 1510 cm^{-1}) suggested an identical Pt binding pattern in both compounds. Second, treatment of the poorly soluble **2** with excess NH_3 gave a mixture of *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2$ and *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2]^{2+}$, as determined by ^1H NMR spectroscopy. The reaction sequence



was consistent with a dinuclear structure of **2**. While structure iv might have yielded *cis*-$(NH_3)_2PtL_2$ and $[Pt(NH_3)_4]^{2+}$ as well, formation of a head–head dimer appeared unlikely under conditions of excess NH_3. Third, when **2** was treated with $[Pt(NH_3)_4]^{2+}$, formation of Magnus' green was not observed.

Similarly, for reactions of the head–head dinuclear complex $[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2](NO_3)_2$ with $K[Pt(NH_3)Cl_3]$ and K_2PtCl_4, respectively, both formation of trinuclear complexes vi and viii and simple anion exchange (vii, ix) could have been expected.

While i and iii have been structurally established in **1** and **2** and IR spectra support vii and ix for the reaction products of the head–head dimers with $[Pt(NH_3)Cl_3]^-$ and $[PtCl_4]^{2-}$, we cannot exclude that any of the other species are formed as well, although we have not been able to isolate them. Moreover, we find that 1-MeT and 1-MeU complexes do not behave strictly analogous. ^1H NMR spectroscopy in fact demonstrates that additional species besides **1** and **2** are formed in low yields. Thus, besides **1** ((80% yield, δ 7.23 (H(6)), 3.34 (N-CH_3), 1.81 and 1.79 ppm (C-CH_3)) two minor products (δ 7.26, 3.32, 1.83 and 7.21, 3.31, 1.76 ppm) appear with time (2 weeks). In the case of the reaction of *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2$ with K_2PtCl_4, three soluble species (H(6) resonances of 1-MeT ligands at δ 7.71, 7.21, and 7.26 ppm) are formed besides the main product **2**, the resonances of which are not detected because of very poor solubility of **2**.

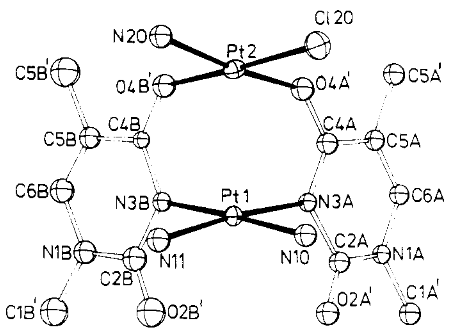


Figure 2. Molecular cation of $[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)Cl][Pt(NH_3)Cl_3]$ (**1**) with atom numbering scheme.

X-ray Structures of 1 and 2. The cation of $[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)Cl][Pt(NH_3)Cl_3]$ (**1**) and the neutral complex $(NH_3)_2Pt(1\text{-}MeT)_2PtCl_2$ (**2**) are depicted in Figures 2 and 3, and selected interatomic distances and angles for both compounds are listed in Tables IV and V. In both compounds, all Pt atoms are square-planar coordinated with Pt1 having a N_4 ligand set. Coordination to the 1-MeT rings is via N3 (Pt1) and via O4 (Pt2). As with other 1-MeT complexes of Pt(II),[6] the O4 and O2 oxygens cannot be differentiated rigorously because of the pseudo C_2 axis going through N3 and C5, but for reasons discussed elsewhere,[6,9c,19]

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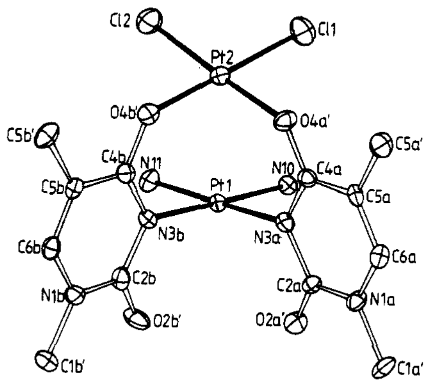

Figure 3. View of *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2PtCl_2$ (**2**).

Table IV. Bond Distances (Å) and Angles (deg) of **1**

(a) Cation			
Pt1-Pt2	2.939 (1)	C4a-C5a	1.41 (3)
Pt1-N10	2.05 (2)	C5a-C5a'	1.55 (3)
Pt1-N11	2.06 (2)	C5a-C6a	1.31 (3)
Pt1-N3a	2.05 (1)	C6a-N1a	1.37 (2)
Pt1-N3b	2.04 (2)	N1b-C1b'	1.49 (3)
Pt2-Cl20	2.28 (1)	N1b-C2b	1.38 (3)
Pt2-N20	2.06 (2)	C2b-O2b'	1.19 (3)
Pt2-O4a'	2.01 (1)	C2b-N3b	1.37 (3)
Pt2-O4b'	2.06 (2)	N3b-C4b	1.39 (2)
N1a-C1a'	1.45 (3)	C4b-O4b'	1.26 (2)
N1a-C2a	1.37 (2)	C4b-C5b	1.42 (3)
C2a-O2a'	1.18 (2)	C5b-C5b'	1.54 (4)
C2a-N3a	1.44 (2)	C5b-C6b	1.31 (3)
N3a-C4a	1.35 (2)	C6b-N1b	1.42 (3)
C4a-O4a'	1.29 (2)		
Pt2-Pt1-N10	100.1 (5)	Pt1-Pt2-Cl20	101.2 (2)
Pt2-Pt1-N11	103.7 (5)	Pt1-Pt2-N20	107.0 (5)
Pt2-Pt1-N3a	81.8 (4)	Pt1-Pt2-O4a'	80.0 (4)
Pt2-Pt1-N3b	82.3 (4)	Pt1-Pt2-O4b'	81.3 (4)
N10-Pt1-N11	90.5 (7)	Cl20-Pt2-N20	92.5 (6)
N10-Pt1-N3a	88.6 (7)	Cl20-Pt2-O4a'	90.0 (5)
N10-Pt1-N3b	177.2 (7)	Cl20-Pt2-O4b'	176.9 (5)
N11-Pt1-N3a	174.5 (7)	N20-Pt2-O4a'	171.9 (7)
N11-Pt1-N3b	87.5 (7)	N20-Pt2-O4b'	88.6 (7)
N3a-Pt1-N3b	93.2 (6)	O4a'-Pt2-O4b'	88.6 (6)
(b) Anion			
Pt3-N30	2.08 (2)	Pt3-Cl31	2.30 (1)
Pt3-Cl3	2.29 (1)	Pt3-Cl32	2.29 (1)
Cl32-Pt3-N30	89.6 (6)	Cl30-Pt3-N30	87.8 (6)
Cl31-Pt3-N30	178.8 (6)	Cl30-Pt3-Cl32	177.3 (3)
Cl31-Pt3-Cl32	90.6 (2)	Cl30-Pt3-Cl31	92.0 (2)

we assume that the oxygen involved in binding Pt2 is O4.

The overall features of the dinuclear complexes **1** and **2** and the dipositive *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2]^{2+}$ cation are very similar, but there are also marked differences in details. The most dramatic one refers to the intracomplex Pt-Pt distance (Table VI). The Pt-Pt separation in **2** is 2.861 (1) Å, which, of all presently characterized diplatinum(II) complexes containing uracil, thymine, or related ligands,[6,20,21] is the shortest one. Specifically, in complexes containing 1-MeU and 1-MeT ligands, Pt-Pt distances usually are above 2.9 Å, except in two complexes with additional metal binding at O2 sites.[5,12] The Pt-Pt distance in **1** is in fact shorter than in some of the partially oxidized Krogmann salts[22] and even shorter than three of the four Pt-Pt separations in a recently described octanuclear platinum(2.25) acetamide complex.[23] Table VI compares several geometrical parameters of all presently known diplatinum(II) complexes containing 1-MeT bridges. It strikes that, unlike in head-tail-oriented 1-MeT ligands, the Pt coordination planes in all three head-head dinuclear complexes are nearly eclipsed. The minimum value of 0.8° is found in **1**. While the relationship between Pt-Pt separation, tilt angle, and torsional angle, as established for dinuclear Pt complexes containing pyridonato ligands,[24] holds up for the three 1-MeT complexes with head-head-oriented ligands, it does not if the compounds with head-tail-oriented 1-MeT ligands are included (cf. discussion in ref 6).

Table V. Bond Distances (Å) and Angles (deg) of **2**

Pt1-Pt2	2.861 (1)	C4a-C5a	1.424 (13)
Pt1-N10	2.064 (10)	C5a-C5a'	1.498 (18)
Pt1-N11	2.055 (8)	C5a-C6a	1.350 (16)
Pt1-N3a	2.027 (7)	C6a-N1a	1.388 (16)
Pt1-N3b	2.025 (9)	N1b-C1b'	1.460 (21)
Pt2-Cl1	2.271 (5)	N1b-C2b	1.374 (17)
Pt2-Cl2	2.278 (3)	C2b-O2b'	1.228 (15)
Pt2-O4a'	2.030 (6)	C2b-N3b	1.365 (17)
Pt2-O4b'	2.009 (10)	N3b-C4b	1.353 (14)
N1a-C1a'	1.476 (16)	C4b-O4b'	1.318 (17)
N1a-C2a	1.356 (12)	C4b-C5b	1.442 (18)
C2a-O2a'	1.204 (15)	C5b-C5b'	1.531 (17)
C2a-N3a	1.379 (14)	C5b-C6b	1.313 (20)
N3a-C4a	1.388 (16)	C6b-N1b	1.388 (15)
C4a-O4a'	1.264 (14)		
Pt2-Pt1-N10	94.3 (3)	Pt1-Pt2-Cl1	101.4 (1)
Pt2-Pt1-N11	93.8 (3)	Pt1-Pt2-Cl2	102.9 (1)
Pt2-Pt1-N3a	84.4 (3)	Pt1-Pt2-O4a'	80.0 (3)
Pt2-Pt1-N3b	84.8 (3)	Pt1-Pt2-O4b'	80.7 (3)
N10-Pt1-N11	92.4 (4)	Cl1-Pt2-Cl2	91.3 (1)
N10-Pt1-N3a	88.8 (4)	Cl1-Pt2-O4a'	88.9 (3)
N10-Pt1-N3b	179.0 (4)	Cl-Pt2-O4b'	176.7 (2)
N11-Pt1-N3a	178.0 (4)	Cl2-Pt2-O4a'	177.0 (3)
N11-Pt1-N3b	88.0 (4)	Cl2-Pt2-O4b'	90.7 (2)
N3a-Pt1-N3b	90.8 (4)	O4a'-Pt2-O4b'	89.0 (3)

Table VI. Comparison of Geometric Parameters of Dinuclear 1-MeT Complexes of Pt(II)

compd	1-MeT arrangement[a]	$Pt-Pt_{intra}$, Å	τ, deg[b]	ω, deg[c]	ref
$[(NH_3)_2Pt(1\text{-}MeT_2Pt(NH_3)_2]^{2+}$	h-h	2.927 (1)	31.4	1.9	6
	h-t	2.947 (1)	36.1	13.8	19a
	h-t	2.920 (1)	35.2	25.7	19b
	h-t	2.915 (1)	30.7	17.9	19b
$[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)Cl]^+$	h-h	2.939 (1)	31.5	0.8	*d*
$(NH_3)_2Pt(1\text{-}MeT)_2PtCl_2 \cdot 3H_2O$	h-h	2.861 (1)	22.5	3.0	*d*

[a] h-h = head-head; h-t = head-tail. [b] Tilt angle between Pt coordination planes. [c] Average torsional angle about Pt-Pt vector. [d] This work.

Pt-N and Pt-O distances in **1** and **2** are in the normal range, but Pt-Cl distances are significantly shorter than in *cis*-$(NH_3)_2PtCl_2$ (2.315 (7), 2.306 (7) Å),[25] consistent with a weaker trans influence of oxygen as opposed to nitrogen. They are, on the other hand, close to values determined in a diplatinum(III) oxidation product of the 1-MeU analogue of **2**, which also has oxygen trans to Cl.[26]

The Pt2 coordination sphere in **1** gives no indication of a disorder between Cl2 and NH_3(20), thus indicating that binding of the $PtCl(NH_3)$ entity to *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2$ leading to **1** takes

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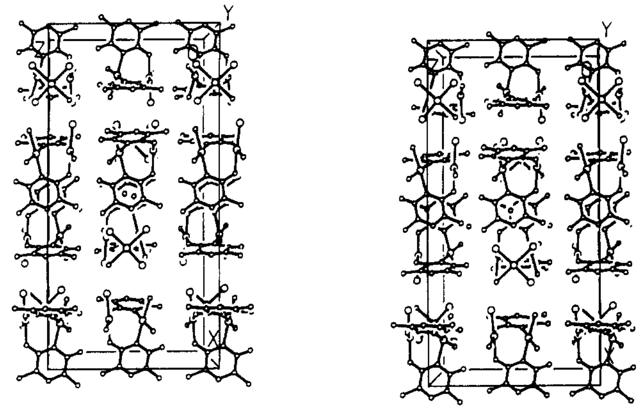

Figure 4. View of the unit cell of **1**.

Table VII. Possible Hydrogen-Bonding Interactions in **1** and **2**

(a) **1**

O10–O10^{1}	3.13		
N20–O2a′^{2}	3.01	Pt2–N20–O2a′^{2}	113
N20–O2b′^{2}	2.82	Pt2–N20–O2b′^{2}	106
N30–O2a′^{3}	3.09	Pt3–N30–O2a′^{3}	111
N11–O10^{4}	3.06	Pt1–N11–O10^{4}	111

Symmetry Operations

(1) $1 - x, 1 - y, 1 - z$
(2) $x, 0.5 - y, -0.5 + z$
(3) $0.5 - x, -y, -0.5 + z$
(4) $-0.5 + x, y, 1.5 - z$

(b) **2**

O10–O11	3.22		
N11–O10^{1}	3.15	Pt1–N11–O10^{1}	119
C11–O10^{2}	3.27	Pt2–C11–O10^{2}	98
O10–O12	2.96		
C12–O12^{4}	3.27	Pt2–C12–O12^{4}	99
O4b′–O11^{5}	3.02	C4b–O4b′–O11^{5}	144
O11–O12^{5}	2.76		
N10–O2a′^{6}	3.21	Pt1–N11–O2a′^{6}	95
N10–O2b′^{6}	3.09	Pt1–N10–O2b′6	153
N11–O2a′^{6}	2.87	Pt2–N20–O2a′^{6}	104
N10–O10^{7}	2.89	Pt2–N10–O10^{7}	117

Symmetry Operations

(1) $x, -1 + y, -1 + z$
(2) $x, y, -1 + z$
(3) $x, y, 1 + z$
(4) $-x, 1 - y, -z$
(5) $-x, 1 - y, 1 - z$
(6) $1 - x, -y, -z$
(7) $1 - x, 1 - y, 1 - z$

place in a stereospecific manner.

Unlike in most cationic diplatinum complexes with N3, O4 metal binding of 1-MeU and 1-MeT ligands, which do not display significant differences in bond lengths of carbonyl groups, there is a clear trend toward differences between coordinating and noncoordinating carbonyl groups in **2**: Of the four groups (C2–O2 = 1.20 (1), 1.23 (1) Å; C4–O4 = 1.26 (1), 1.32 (1) Å) to be compared, three differences in bond lengths are significant (4.3σ–8.5σ)[27] and in agreement with an expected lengthening of the CO group on metal binding.

The geometry of the $[Pt(NH_3)Cl_3]^-$ anion of **1** is normal and compares well with literature data.[28]

Figure 4 gives a view of the unit cell of **1**. Dinuclear cations form infinite strands parallel to the *z* axis with hydrogen bonding between $NH_3(20)$ and exocyclic O2 oxygens of the adjacent cation (Table VII). Intermolecular Pt···Pt separations are 4.280 Å, and angles between intracomplex and intercomplex Pt···Pt vectors are 156.14 (Pt1) and 173.45° (Pt2). Along the *y* axis, 1-MeT rings (b) of adjacent cations alternatively stack and point away from each other.

Apart from hydrogen bonding of the three water molecules in **2** with the diplatinum(II) complex, which is extensive (Table VII), there is also hydrogen bonding between pairs of molecules via exocyclic O2 oxygens and NH_3 groups. The shortest intermolecular Pt1–Pt1′ separation is 4.49 Å.

Related Complexes. $(bpy)Pt(1\text{-}MeT)_2PtCl_2\cdot 3H_2O$ (**3**) and $(bpy)Pt(1\text{-}MeT)_2PdCl_2\cdot 2H_2O$ (**4**) are analogues of **2** and have been prepared in a similar way, as has been the previously reported[10b] *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2PdCl_2$. The structural assignment as 1-MeT (1-MeU) bridged (N3,O) dinuclear complexes in all cases was based on IR spectroscopic criteria, in particular the characteristic, intense modes at ca. 1660 and 1510–1530 cm^{-1} and the presences of ν(M–Cl) absorptions around 340 cm^{-1}. Attempts to prepare the Pd_2 analogues of **2** failed. Although we have isolated two compounds of analytical composition $A_2Pd(1\text{-}MeT)_2PdCl_2\cdot aq$ (A_2 = en, bpy), the IR spectra (intense band at 1550–1570 cm^{-1}, no band at 1510–1530 cm^{-1}) rule aganst N3,O4 metal binding to 1-MeT. We conclude this from a comparison with the structurally characterized $[(bpy)Pd(1\text{-}MeT\text{-}N^3,O^4)_2Pd(bpy)]^{2+}$ (head–head),[29] the IR spectrum of which fully confirms the arguments used above.

Anion Exchange. $[Pt(NH_3)Cl_3]^-$ and $[PtCl_4]^{2-}$ apparently do not form trinuclear species of types vi and vii (Figure 1) when mixed with the head–head dimer *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2](NO_3)_2$ but rather displace the nitrates and precipitate the Pt_2 species as $[Pt(NH_3)Cl_3]^-$ (**6**) and $[PtCl_4]^{2-}$ (**5**) salts. The cation modes in the IR spectra are quite conclusive in this respect.

Solution Behavior of 2. *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2PtCl_2\cdot 3H_2O$ (**2**) is virtually insoluble in water. However, in a slow process, which is accompanied by a drop in pH, **2** undergoes hydrolysis.[30] The resulting brownish yellow solution (λ_{max} at 282 and 426 nm) darkens with time (days) to give an almost black solution (visible absorptions at ca. 445, 560, and 685 nm). On evaporation, brown-black glasses are obtained that exhibit broad and prominent IR absorptions at 1650 and 1520 cm^{-1} and a weaker one around 1570 cm^{-1}. These features are consistent with N3,O metal bridging largely maintained, as confirmed by the position of the UV absorption.[7] Interestingly, addition of excess NaCl to a solution of aged **2** does not regenerate **2**.

Samples of **2** treated with 2 equiv of $AgNO_3$ in water display rather similar, albeit not fully identical UV–vis spectra. ^1H NMR indicate the presence of a major product and several (6?) minor ones. The main product is not identical with any of the following species: 1-MeTH, *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2$, *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2]^{2+}$ (head–head or head–tail). Studies are presently underway to better understand the solution chemistry of **2** and the oxidizability of **1** and **2**.

Acknowledgment. We acknowledge, with thanks, support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie and G. Trötscher for her assistance with the X-ray work.

Supplementary Material Available: Listings of positional and thermal parameters and dihedral angles for **1** and **2** and figures showing IR spectra of *cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2Pt(NH_3)_2](NO_3)_2$, **1**, and **2** (7 pages); listings of observed and calculated structure factors for **1** and **2** (38 pages). Ordering information is given on any current masthead page.

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(27) σ is defined as $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$ with σ_1 and σ_2 being the errors in bond lengths compared.

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(30) 70 mg of **2** "dissolve" in 200 mL of H_2O within 20 h at 22 °C, pH 4.5. The process appears to be largely irreversible, since subsequent concentration to a 10-mL volume affords less than 5 mg of **2**.