surface. Under conditions where the surface coverage of $Fe(CO)_5$ does not exceed one monolayer, $Fe_3(CO)_{12}$ is the only photoproduct observed spectroscopically. If the surface coverage of $Fe(CO)_5$ greatly exceeds one monolayer, $Fe_2(CO)_9$ is also an important product and appears to be aggregated rather than dispersed on the support surface. The mechanism for the formation of $Fe_3(CO)_{12}$ appears to involve the initial formation of surface-bound $Fe(CO)_4$, which undergoes subsequent thermal trimerization on the silica surface.

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Registry No. $Fe(CO)_5$, 13463-40-6; $Fe_3(CO)_{12}$, 17685-52-8; CO, 630-08-0; silica, 7631-86-9.

Bis(1-methyluracilato-N^3)-*cis*-diammineplatinum(II)-4-Water and Bis(μ-1-methyluracilato-N^3,O^4)-*cis*-diammineplatinum(II)diaquocopper(II) Sulfate-4.5-Water (Head-Head). Preparation, Crystal Structures, and Implications for the Formation of Heteronuclear Pt,M Complexes

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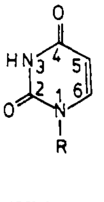
Contribution from the Anorganisch-Chemisches Institut der Technischen Universität München, 8046 Garching, FRG. *Received February 24, 1982*

Abstract: The syntheses and crystal structures of two complexes of 1-methyluracil are reported. *cis*-$Pt(NH_3)_2(1\text{-MeU})_2\cdot 4H_2O$ (**2**) crystallizes in space group $C2/c$ with cell parameters a = 26.822 (14) Å, b = 7.030 (2) Å, c = 20.044 (9) Å, and β = 96.36 (4)° and has eight formula units in the unit cell. The structure was refined on 2416 reflections to R_1 = 0.038 and R_2 = 0.044. 1-Methyluracil anion ligands, 1-MeU, exhibit N3 platinum binding and are arranged in head-tail fashion. With Cu(II), **2** forms heteronuclear complexes of Pt:Cu = 1:1 and 2:1 stoichiometries, depending upon the applied Pt:Cu ratio *and* the anions present. The crystal structure of one of these complexes has been determined. *cis*-$[Pt(NH_3)_2(1\text{-MeU})_2Cu(H_2O)_2]SO_4\cdot 4.5H_2O$ (**4**) crystallizes in space group $P\bar{1}$ with cell parameters a = 10.398 (10) Å, b = 10.773 (8) Å, c = 11.772 (9) Å, α = 102.88 (6)°, β = 102.62 (7)°, and γ = 105.05 (7)° and has two formula units in the unit cell. The structure was refined on 3028 reflections to R_1 = 0.091 and R_2 = 0.096. Pt and Cu have square-planar coordination spheres and are linked through two 1-MeU ligands in a head-head arrangement, binding to Pt via N3 and to Cu via O4. The coordination spheres are completed by two NH_3 ligands (Pt) and two H_2O groups (Cu), each in cis arrangements. The Pt-Cu distance within the cation is 2.765 (3) Å. Related heteronuclear Pt,Cu complexes of 2:1 stoichiometries and varying anions have been prepared and reasons for their formation are discussed. Possibilities for the formation of homonuclear Pt_x and heteronuclear Pt_x,M_y complexes with long metal chains are outlined.

Introduction

1-Methyluracil can be considered a model of the naturally occurring RNA base uridine and the DNA base thymidine. Its metal coordination properties, like those of the other nucleic acid components, are of interest with respect to nucleic acid replication,[1] mutagenesis,[2] carcinogenesis,[3] antitumor activity,[4] and heavy-metal labeling of nucleic acids.[5] N1-substituted uracil contains several potential donor atoms for metal coordination—N3, O4, O2, C5, and combinations of these[6-10] —most of which are documented in the literature (Chart I). With unsubstituted uracil the number of possible coordination sites is even larger.[11] Recently, we made extensive use of the excellent ligating properties of N3-platinated pyrimidine-2,4-diones via their exocyclic oxygen atoms, specifically of complexes of composition *cis*-$Pt(NH_3)_2(1\text{-MeU})_2$ and *cis*-$Pt(NH_3)_2(1\text{-MeT})_2$,[12] which lead to di-[13] and heteronuclear Pt,M

Chart I



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(12) Abbreviations used: 1-MeU = monoanion of 1-methyluracil; 1-MeT = monoanion of 1-methylthymine; 1-MeUH = neutral 1-methyluracil.

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complexes.[9,14,15] We attributed this property, as well as the easy protonation of these complexes,[16] to the fact that platinum substitution for the proton at N3 releases electron density into the heterocyclic ring, thus increasing the basicity of the keto oxygens. These conclusions are in agreement with the suggestions of Guay and Beauchamp on complex formation of 1-methylthymine with Ag[17] and CH_3Hg/Na.[18] A similar interpretation could be evoked to explain to formation of dimeric head–tail platinum(II) complexes of 1-methyluracil and 1-methylthymine as described by Lock, Rosenberg, and co-workers[8,19] and ourselves.[20]

Reaction of *cis*-$Pt(NH_3)_2(1\text{-MeU})_2$ with a heterometal ion such as Cu(II) was considered a method of probing the relative basicities of the exocyclic O4 and O2 atoms, respectively. It had been anticipated by us that an effective C_2 symmetry of *cis*-$Pt(NH_3)_2(1\text{-MeU})_2$ in the solid state, combined with our findings on N3,O4 bridging in the Pt,Cu complex described here as well as in the head–head Pt dimer[21] and the pentanuclear Pt_4,Ag complex[9] might be another hint that O4 indeed is more basic than O_2. Formation of the N3,O4-bridged Pt,Cu complex consequently requires rotation of one of the two 1-MeU ligands of *cis*-$Pt(NH_3)_2(1\text{-MeU})_2$. Our findings do not rule out the existence of N3,O2 bridging but indicate a greater stability of a N3,O4 bridge.

cis-$Pt(NH_3)_2(1\text{-MeU})_2$ represents a model of a hypothetical interaction of the antitumor agent *cis*-$Pt(NH_3)_2Cl_2$ with two uridine (RNA) or thymidine (DNA) ligands. Even though there is at present no hard evidence to believe that such a product is of biological significance, it is of interest with regard to the recent work of Orbell, Marzilli, and Kistenmacher[22] on conformational features of bis(nucleobase) complexes of cis Pt(II) and the interactions of the exocyclic groups of the heterocyclic rings with each other.[23]

The reported dinuclear mixed Pt,Cu complex is a model of a simultaneous interaction of two different metal ions with a nucleobase. Complexes of this type may be of interest with regard to magnetic properties, exchange coupling phenomena, and intramolecular electron-transfer processes[24] besides their possible biochemical relevance.

Experimental Section

Reagents and Preparations. *cis*-$Pt(NH_3)_2Cl_2$ was prepared from K_2PtCl_4 (Degussa) according to the method described by Dhara[25] and recrystallized from DMF/HCl. 1-Methyluracil was obtained from Vega Biochemicals.

***cis*-$Pt(NH_3)_2(1\text{-MeU})_2 \cdot nH_2O$ (n = 2, 4) (1, 2).** A 15-mmol amount of *cis*-$[Pt(NH_3)_2(H_2O)_2](NO_3)_2$ in 90 mL of water, prepared in situ from *cis*-$Pt(NH_3)_2Cl_2$ with use of $AgNO_3$, was stirred with 60 mmol of 1-methyluracil and 30 mmol of NaOH (150 mL of 0.2 N NaOH) for 40 h at 60 °C and 24 h at 22 °C. The solution (pH 8) was filtered from a few milligrams of an unidentified precipitate and concentrated to a 60-mL volume on a Rotavapor. A 7.5-g quantity of precipitate (A), consisting of **2** and 1-MeUH[12] was filtered, air-dried, and treated with 400 mL of MeOH for 40 h at 22 °C. The undissolved material consisted of 5.2 g of *cis*-$Pt(NH_3)_2(1\text{-MeU})_2 \cdot 2H_2O$ (**1**), yield 67%. Anal. Calcd: C, 23.30; H, 3.92; N, 16.31; Pt, 37.85. Found: C, 23.14; H, 3.97; N, 16.28; Pt, 37.70. As evident from IR and ^1H NMR spectra, the compound was free of MeOH and 1-MeUH. Recrystallization of the dihydrate from water gave the tetrahydrate **2** as transparent crystals that rapidly lose water of crystallization when kept in air. Anal. Calcd: C, 21.78; H, 4.40; N, 15.24; Pt, 35.37. Found: C, 21.54; H, 4.33; N, 15.08; Pt, 35.4. The filtrate obtained after filtration of A was brought to pH 5 by means of HNO_3 and allowed to evaporate. One gram of unreacted 1-MeUH was collected before the solution solidified. The solid (4.9 g) was stirred in 250 mL of MeOH and filtered after 30 min at 22 °C, when almost all had dissolved. Stirring of the clear, transparent solution for 24 h resulted in formation of white, glistening crystals (1.6 g, yield 20%/Pt), which was analyzed as $Pt(NH_3)_2(1\text{-MeU})_2 \cdot 0.5NaNO_3 \cdot 1.5H_2O$ (**3**). Anal. Calcd: C, 21.88; H, 3.50; N, 16.59. Found: C, 21.92; H, 3.33; N, 16.34.

A $NaNO_3$ adduct of *cis*-$Pt(NH_3)_2(1\text{-MeU})_2$ was also obtained as follows: 250 mg of **1** treated with 50 mL of a MeOH solution saturated with $NaNO_3$. Althrough **1** is rather insoluble in MeOH alone, it readily dissolves in MeOH/$NaNO_3$. Within 1 day at 22 °C 60 mg of white, glistening microneedles precipitated. They were filtered, washed with MeOH, and air-dried. The IR spectrum indicates the presence of NO_3^- and so does elemental analysis (approximately 1 $NaNO_3$/Pt)[26]. The compound does not contain MeOH as evident from an NMR spectrum. X-ray powder patterns of the two $NaNO_3$ adducts and of $NaNO_3$ alone were taken and compared. They proved that the two adducts are not identical and do not represent admixtures of **2** and $NaNO_3$.

***cis*-$[(NH_3)_2Pt(1\text{-MeU})_2Cu(H_2O)_2]SO_4 \cdot 4.5H_2O$ (4).** A 1-mmol quantity of **2** and 4 mmol of $CuSO_4 \cdot 5H_2O$ were cocrystallized at 22 °C (pH 3.93). Several fractions of blue-green crystal plates were collected; total yield 87%. The identical compound was also obtained when the applied Pt:Cu ratio was 1 instead of 0.25. However, then also a small amount of **5** was obtained. Anal. Calcd: C, 15.91; H, 3.88; N, 11.13; Cu, 8.41. Found: C, 16.47; H, 3.98; N, 11.00; Cu, 8.6.

***cis*-$[(NH_3)_2Pt(1\text{-MeU})_2Cu(1\text{-MeU})_2Pt(NH_3)_2]SO_4 \cdot 12H_2O$ (5).** A 1-mmol quantity of **2** and 0.25 mmol of $CuSO_4 \cdot 5H_2O$ were cocrystallized from an aqueous solution (pH 6.8). After filtration of 240 mg of **2**, 200 mg of **5** was obtained: yellowish green octahedrons; yield 36%/Pt. Anal. Calcd: C, 18.00; H, 4.24; N, 12.80; Cu, 4.76. Found: C, 17.74; H, 4.27; N, 13.25; Cu, 4.7. The crystals readily lose water of crystallization to get a deeper green color.

***cis*-$[(NH_3)_2Pt(1\text{-MeU})_2Cu(1\text{-MeU})_2Pt(NH_3)_2](NO_3)_2 \cdot 6H_2O$ (6).** **2** and $Cu(NO_3)_2 \cdot 3H_2O$ were cocrystallized from aqueous solution. Regardless of the Pt:Cu ratio (1:1 or 1:4), only the Pt_2,Cu product was obtained. Anal. Calcd: C, 19.15; H, 3.54; N, 15.63; Cu, 5.06. Found: C, 19.02; H, 3.59; N, 15.84; Cu, 5.33.

***cis*-$[(NH_3)_2Pt(1\text{-MeU})_2Cu(1\text{-MeU})_2Pt(NH_3)_2]Cl_2 \cdot 10H_2O$ (7).** A 0.14-mmol quantity of **4** was dissolved in 5 mL of H_2O (pH 5). Excess NaCl (100 mg) was added and the solution kept at 22 °C. After 1 day 40 mg of **7** was filtered as yellow, transparent microplates. When the solution was dry, a mixture of **7**, NaCl, and $CuCl_2$ was obtained. Brief treatment with 2 mL of H_2O dissolved all NaCl and $CuCl_2$ to give 20 mg of **7**. Anal. Calcd: C, 18.86; H, 4.12; N, 13.20; Cu, 4.99. Found: C, 18.98; H, 3.94; N, 13.08; Cu 5.15. As compared with the corresponding SO_4^{2-} and NO_3^- salts **5** and **6**, the Cl^- salt **7** is rather insoluble in water.

***cis*-$[(NH_3)_2Pt(1\text{-MeU})_2Cu(1\text{-MeU})_2Pt(NH_3)_2]PtCl_4 \cdot 6H_2O$ (8).** A 0.2-mmol quantity of **4** was dissolved in 10 mL of H_2O, and 0.2 mmol of K_2PtCl_4, dissolved in 1.5 mL of H_2O, was added dropwise. The color of the solution rapidly changed from greenish yellow to yellow, and rapidly a yellow precipitate formed (pH 4). The precipitate was filtered, washed with water, and dried under high vacuum; yield 140 mg. **8** does not contain SO_4^{2-} as was evident from an IR spectrum. ν(Pt–Cl) occurs at 320 cm^{-1}. Anal. Calcd: C, 16.48; H, 3.05; N. 11.54; Cu, 4.36; Cl, 9.73. Found: C, 16.40; H, 2.87; N, 11.71; Cu, 4.6; Cl, 10.04.

Spectra. IR spectra were recorded on a Perkin-Elmer 580 grating spectrometer (maximum resolution 2.8 cm^{-1}) as KBr pellets and Nujol mulls (CsI windows). Differences in respective absorptions were small, but with KBr samples of **4** a color change to brown was observed. ^1H NMR spectra were recorded on a JEOL JNM-FX 60 spectrometer in D_2O with $[N(CH_3)_4]BF_4$ as internal standard. Shifts are quoted on the δ scale and are calculated relative to TSP (sodium 3-(trimethylsilyl)propanesulfonate), with TSP 3.1869 ppm upfield of $[N(CH_3)_4]^+$. pD values were obtained by adding 0.4 unit to the pH meter reading.

Crystallography. Crystals of **2** and **4** (approximately 0.6 × 0.3 × 0.3 mm each) were sealed in glass capillaries, and precession photographs were taken. So that loss of water of crystallization could be avoided, **2** was sealed in the presence of a drop of water. **2** crystallizes in the

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(26) Anal. Found: C, 19.56; H, 3.38; N, 15.36. This gives C:H:N = 10:20.5:6.8.

Table I. Crystal Data for *cis*-$Pt(NH_3)_2(1\text{-}MeU)_2 \cdot 4H_2O$ (2) and *cis*-$[Pt(NH_3)_2(1\text{-}MeU)_2Cu(H_2O)_2]SO_4 \cdot 4.5H_2O$ (4) (1-MeU = $C_5H_5N_2O_2$)

	2	4
a, Å	26.822 (14)	10.398 (10)
b, Å	7.030 (2)	10.773 (8)
c, Å	20.044 (9)	11.772 (9)
α, deg	90.0	102.88 (6)
β, deg	96.36 (4)	102.62 (7)
γ, deg	90.0	105.05 (7)
V, Å^3	3756.2	1186.5
space group	*C*2/*c*	$P\bar{1}$
Z	8	2
D_{measd}, g cm^{-3}	1.96	2.10
D_{calcd}, g cm^{-3}	1.95	2.12
linear abs coeff, cm^{-1}	79.1	72.9
emp abs cor	yes	yes
no. of measd reflctns	3247	3726
no. of obsd reflctns	2416	3721
struct factor	2416	3028
F_o	$\geqslant 3.92\sigma_{F_o}$	$\geqslant 4.5\sigma_{F_o}$
R_1[a]	0.038	0.091
R_2[a]	0.044	0.096
temp, K	295	295

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma F_o$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$.

Table II. Atomic Positional Parameters of 2 (×10^4)

atom	*x*/*a*	*y*/*b*	*z*/*c*
Pt	1887.7 (1)	1047.6 (5)	−1982.3 (2)
N10	2405 (3)	3127 (12)	−2125 (4)
N20	1529 (3)	1524 (12)	−2925 (4)
N3A	1385 (2)	−1048 (12)	−1852 (4)
C2A	895 (4)	−510 (15)	−1806 (5)
O2A	740 (2)	1117 (12)	−1915 (4)
N1A	567 (3)	−1850 (14)	−1607 (5)
C11A	50 (4)	−1281 (22)	−1504 (9)
C6A	716 (4)	−3761 (18)	−1534 (6)
C5A	1187 (4)	−4313 (15)	−1602 (6)
C4A	1552 (4)	−2876 (15)	−1754 (4)
O4A	1998 (3)	−3266 (12)	−1799 (4)
N3B	2227 (3)	576 (10)	−1029 (4)
C2B	2714 (4)	20 (14)	−941 (5)
O2B	2973 (3)	195 (12)	−1418 (4)
N1B	2926 (3)	−406 (13)	−297 (5)
C11B	3454 (4)	−972 (20)	−193 (6)
C6B	2655 (4)	−217 (16)	247 (5)
C5B	2183 (4)	349 (16)	153 (6)
C4B	1948 (4)	837 (14)	−497 (5)
O4B	1519 (3)	1489 (12)	−603 (4)
O1	5000 (0)	1717 (18)	2500 (0)
O2	4374 (4)	774 (15)	3452 (5)
O3	3755 (3)	2638 (16)	−1428 (4)
O4	752 (4)	1183 (16)	174 (6)
O5	4740 (6)	2445 (26)	4700 (8)

monoclinic system with the absences of *C*2/*c* or *Cc*, whereas **4** is triclinic. For **2** the centrosymmetric space group was assumed and confirmed by the successful solution of the structure. Unit cell parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 reflections for the two crystals in the range 15° < 2θ < 25° recorded on a Syntex P2$_1$ diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å at 22 °C). Crystal data and other numbers related to data collection are summarized in Table I. Densities were obtained by flotation in a CH_3I/CCl_4 mixture. Intensity data were recorded on a Syntex P2$_1$ diffractometer with the ω scan. For the calculation of the structure factors corrections of the Lorentz-polarization effects and the absorption were made.

Both structures were solved with use of the Syntex XTL system. The coordinates of the platinum atoms of **2** and **4** as well as those of the copper atom in **4** were obtained from three-dimensional Patterson syntheses. A series of full-matrix least-squares refinements, followed by three-dimensional electron density difference syntheses, gave all non-hydrogen atoms. The refinements using full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ were terminated when the maximum shift/error was about 0.1. For compound **2** all atoms except the water molecules were refined anisotropically; with **4** only Pt, Cu, and S atoms were refined anisotropically. The atom parameters of **2** and **4** are listed in Table II and III. Five positions of water molecules were detected for **2**: the oxygen atom O1 lies on a special position (2-fold axis), and the temperature factor of the oxygen atom O5 indicated an occupancy of 0.5.

Five positions of water molecules (coordinated water not counted) were detected for **4**, with one oxygen (O55) having a temperature factor typical of a 50% occupancy.

The sulfate oxygens are disordered, and the difference Fourier syntheses showed eight oxygens that could be refined isotropically. On the basis of O–S–O angles, the disordered sulfates occur as S, O31, O33, O34, O37 and as S, O32, O35, O36, O37.

Powder Patterns of $NaNO_3$ Adducts. X-ray powder patterns of the two $NaNO_3$ adducts of *cis*-$Pt(NH_3)_2(1\text{-}MeU)_2$ were taken on a Siemens D-500 diffractometer using graphite-monochromated Cu Kα radiation.

Table III. Atomic Positional Parameters of 4 (×10^3)[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*
Pt	209.8 (1)	187.9 (1)	31.6 (1)
Cu	462.3 (3)	340.0 (3)	18.9 (2)
N3C	155 (2)	179 (2)	−144 (2)
C4C	252 (3)	225 (3)	−208 (3)
O4C	378 (2)	271 (2)	−155 (2)
C5C	198 (3)	210 (3)	−334 (3)
C6C	59 (3)	160 (3)	−390 (3)
N1C	−31 (2)	116 (2)	−328 (2)
C11C	−183 (3)	52 (3)	−394 (3)
C2C	13 (2)	121 (2)	−205 (3)
O2C	−70 (2)	79 (2)	−152 (2)
N3D	186 (2)	368 (2)	84 (2)
C4D	268 (2)	485 (2)	75 (2)
O4D	376 (1)	483 (2)	36 (1)
C5D	242 (3)	608 (3)	110 (3)
C6D	132 (3)	607 (3)	152 (3)
N1D	50 (2)	490 (2)	164 (2)
C11D	−76 (3)	485 (3)	208 (3)
C2D	69 (3)	370 (3)	130 (3)
O2D	−1 (2)	267 (2)	142 (2)
N30	226 (2)	1 (2)	−20 (2)
N40	259 (2)	185 (2)	205 (2)
O1	570 (2)	414 (2)	192 (2)
O2	563 (2)	201 (2)	7 (2)
S	580.4 (8)	94.8 (8)	269.6 (8)
O31	541 (4)	222 (4)	307 (4)
O32	510 (4)	42 (4)	141 (4)
O33	441 (4)	−23 (4)	189 (4)
O34	664 (5)	111 (5)	191 (5)
O35	707 (5)	52 (5)	275 (5)
O36	506 (7)	54 (6)	345 (6)
O37	647 (7)	61 (6)	370 (6)
O38	634 (6)	244 (5)	304 (5)
O51	504 (2)	572 (2)	368 (2)
O52	489 (2)	820 (2)	421 (2)
O53	282 (3)	414 (3)	424 (3)
O54	967 (3)	176 (3)	338 (3)
O55	161 (5)	613 (5)	497 (5)

[a] The atoms O31–O38 and O55 have an occupancy factor of 0.5.

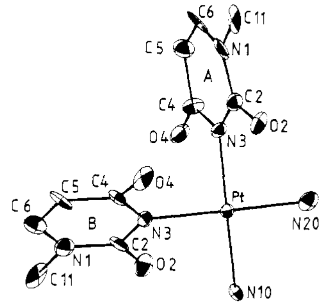

Figure 1. The molecule *cis*-$Pt(NH_3)_2(1\text{-}MeU)_2$.

Results

Crystal Structure of *cis*-$Pt(NH_3)_2(1\text{-}MeU)_2 \cdot 4H_2O$. The molecule is shown in Figure 1, interatomic distances and angles are given in Table IV, and conformational parameters are given in Table V. Pt(II) is square-planar coordinated with normal bond

Table IV. Interatomic Distances (Å) and Angles (Deg) for *cis*-Pt$(NH_3)_2$(1-MeU)$_2$·4H_2O

(a) Pt Coordination Sphere

Pt-N10	2.057 (8)	Pt-N3A	2.034 (8)
Pt-N20	2.050 (9)	Pt-N3B	2.050 (8)
N10-Pt-N20	90.6 (4)	N20-Pt-N3A	89.3 (3)
N10-Pt-N3A	178.8 (3)	N20-Pt-N3B	178.4 (3)
N10-Pt-N3B	90.5 (3)	N3A-Pt-N3B	89.7 (3)

(b) 1-Methyluracilato Ligands

	ring A	ring B
N1-C11	1.478 (16)	1.464 (16)
N1-C2	1.380 (15)	1.379 (15)
C2-O2	1.229 (14)	1.247 (14)
C2-N3	1.378 (14)	1.365 (15)
N3-C4	1.368 (14)	1.382 (14)
C4-O4	1.240 (15)	1.237 (14)
C4-C5	1.463 (17)	1.424 (16)
C5-C6	1.342 (18)	1.321 (19)
C6-N1	1.405 (17)	1.382 (16)
N3-C2-N1	118.4 (10)	118.1 (10)
N3-C2-O2	123.4 (10)	122.5 (10)
N1-C2-O2	118.2 (10)	119.4 (10)
C2-N3-C4	123.2 (9)	122.2 (9)
C2-N3-Pt	117.4 (7)	119.3 (7)
C4-N3-Pt	119.2 (7)	118.4 (7)
N3-C4-C5	117.5 (10)	116.9 (10)
N3-C4-O4	120.1 (10)	119.3 (10)
O4-C4-C5	122.4 (10)	123.8 (10)
N1-C6-C5	121.8 (12)	119.6 (11)
C6-C5-C4	118.7 (11)	121.6 (11)
C2-N1-C11	119.7 (10)	118.6 (10)
C11-N1-C6	120.4 (11)	119.8 (10)
C2-N1-C6	119.9 (10)	121.5 (10)

Table V. Conformational Parameters of *cis*-Pt$(NH_3)_2$(1-MeU)$_2$·4H_2O[a]

(a) Dihedral Angles (Deg)

(N10, N20, N3A, N3B)/ring A	112.5
(N10, N20, N3A, N3B)/ring B	119.3
ring A/ring B	109.0

(b) Deviation of Pt from Least-Squares Planes of Rings A and B (Å)

ΔPt(ring A)	+0.229	ΔPt(ring B)	+0.117

[a] Equations of planes: Primary Pt coordination plane (N10, N20, N3A, N3B), $0.6391X - 0.6770Y - 0.3651Z = 4.4601$; Ring A, $-0.1502X - 0.1832Y - 0.9715Z = 3.1039$; Ring B, $-0.2998X - 0.9476Y - 0.1106Z = -2.0279$.

angles and normal Pt–NH_3 and Pt–N(1-MeU) distances.[8,9] The dihedral angle between the two 1-MeU rings is 109°, and the angles between the Pt coordination plane and the uracil planes are 112.5 (A) and 119.3° (B). The two rings are oriented in a way that O4A and O4B, and likewise the O2 groups, are at opposite sites of the Pt coordination plane, thus leading to an approximate C_2 symmetry of the molecule. Pt lies significantly out of the planes of rings A (+0.229 Å) and B (+0.117 Å), similar to the case for Hg in Hg(1-MeT)$_2$[27] or for Pt in a heteronuclear complex with Ag.[14] The 1-MeU rings are essentially planar. Bond lengths and angles within the rings do not differ significantly. As compared with the situation in neutral 1-methyluracil,[28] no significant changes in bond lengths can be seen, but there is a trend in changes in internal bond angles in the vicinity of the Pt coordination site (decrease of the angle at N3 and slight increases in the angles at C2 and C4) as expected[29] and as previously seen in Pt complexes of uracil and thymine ligands.[8,19,30]

Table VI. Possible Hydrogen Bonds Involving the Exocyclic Oxygens of the 1-MeU and NH_3 Ligands in *cis*-Pt$(NH_3)_2$(1-MeU)$_2$[a]

O2A-H_2O(1)	2.669 (11)	C2A-O2A-O1	146.2 (8)
O2B-N20[b]	3.038 (12)	Pt-N20-O2B	109.9 (4)
-N10[b]	3.209 (12)	Pt-N10-O2B	103.8 (3)
-H_2O(3)	2.895 (14)	C2B-O2B-O3	113.8 (7)
O4A-N10[c]	2.865 (12)	Pt-N10-O4A	108.5 (4)
-N10[b]	2.990 (12)	Pt-N10-O4A	106.9 (4)
O4B-H_2O(4)	2.721 (15)	C4B-O4B-O4	128.4 (8)
N10-O4A[d]	2.865 (12)		
-O4A[e]	2.990 (12)		
-O2B[e]	3.209 (12)		
N20-O2B[e]	3.038 (12)		
-H_2O(2)	3.167 (15)	Pt-N20-O2	132.0 (4)
-H_2O(3)[b]	3.084 (14)	Pt-N20-O3	108.2 (4)

[a] Symmetry transformations are indicated by footnotes *b*–*e*. Distances are given in angstroms and angles in degrees. [b] $0.5 - x, -0.5 + y, -0.5 - z$. [c] $x, -1 + y, -1 + z$. [d] $x, 1 + y, z$. [e] $0.5 - x, 0.5 + y, -0.5 - z$.

Table VII. Selected Interatomic Distances (Å), Angles (Deg), and Possible Hydrogen-Bonding Interactions in *cis*-[$(NH_3)_2$Pt(1-MeU)$_2$Cu$(H_2O)_2$]SO_4·4.5H_2O[a]

(a) Distances and Angles around the Metals

Pt-N3	2.03 (2)	Cu-O4C	1.92 (2)
-N4	2.00 (2)	-O4D	1.97 (2)
-N3C	2.00 (2)	-O1	1.96 (2)
-N3D	2.00 (2)	-O2	2.04 (2)
Pt-Cu	2.765 (3)		
N30-Pt-N40	88.9 (9)	N40-Pt-N3C	176.7 (8)
N30-Pt-N3C	88.5 (9)	N40-Pt-N3D	90.2 (9)
N30-Pt-N3D	177.5 (9)	N3C-Pt-N3D	92.3 (8)
O1-Cu-O2	87.4 (8)	O2-Cu-O4C	88.9 (8)
O1-Cu-O4D	90.2 (7)	O2-Cu-O4D	176.7 (8)
O1-Cu-O4C	173.3 (8)	O4C-Cu-O4D	83.4 (7)

(b) Intermolecular Metal-Metal Distances

Pt-Pt[b]	4.903 (2)	Cu-Cu[c]	3.483 (5)

(c) Possible Hydrogen Bonds Involving O2 of 1-MeU, NH_3, and H_2O Ligands

H_2O(1)-O31	2.71 (5)	Cu-O1-O31	111.4 (12)
-O38	2.62 (6)	Cu-O1-O38	117.2 (15)
-O51	2.71 (3)	Cu-O1-O51	126.2 (10)
H_2O(2)-O32	2.60 (5)	Cu-O2-O32	113.5 (14)
-O32[d]	2.61 (5)	Cu-O2-O32	131.2 (15)
-O33[d]	2.64 (5)	Cu-O2-O33	128.6 (14)
-O34	2.68 (6)	Cu-O2-O34	125.2 (15)
N3-O2D[b]	3.01 (3)	Pt-N3-O2D	129.4 (11)
-O32	3.00 (4)	Pt-N3-O32	101.7 (11)
-O33	3.05 (5)	Pt-N3-O33	107.5 (11)
-O34[d]	2.73 (6)	Pt-N3-O34	131.4 (13)
-O35[d]	3.19 (6)	Pt-N3-O35	110.5 (11)
N4-O2C[b]	2.85 (3)	Pt-N4-O2C	94.2 (9)
-O31	2.80 (5)	Pt-N4-O31	114.0 (13)
-O33	3.29 (5)	Pt-N4-O33	100.1 (11)
-O53	3.06 (4)	Pt-N4-O53	124.8 (10)
O2C-N40[b]	2.85 (3)	Pt-N40-O2C	94.2 (9)
-N30[b]	3.00 (3)	Pt-N30-O2C	89.4 (8)
O2D-N30[b]	3.01 (3)	Pt-N30-O2D	129.4 (11)
-O54[e]	2.75 (4)	C2C-O22-O54	134.9 (19)

[a] Symmetry transformations are indicated by footnotes *b*–*e*. [b] $-x, -y, -z$. [c] $1 - x, 1 - y, -z$. [d] $1 - x, -y, -z$. [e] $-1 + x, y, z$.

There is extensive hydrogen bonding between the exocyclic oxygens of the 1-MeU rings and water molecules and NH_3 groups (Table VI): the O2 atoms of both rings are strongly hydrogen bonded to H_2O molecules (2.669 (11) (A) and 2.895 (14) Å (B)) and have weaker intermolecular hydrogen bonds with NH_3 groups (3.05–3.20 Å). Of the O4 atoms, only O4B is strongly hydrogen bonded to a water molecule (2.721 (15) Å), whereas O4A is intermolecularly hydrogen bonded to NH_3 ligands.

Crystal Structure of *cis*-[$(NH_3)_2$Pt(1-MeU)$_2$Cu$(H_2O)_2$]SO_4·4.5H_2O. A pair of centrosymmetrically related cations of 4 is shown in Figure 2. Selected interatomic distances and possible

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(27) Kosturko, L. D.; Folzer, C.; Stewart, R. F. *Biochemistry* **1974**, *13*, 3949.

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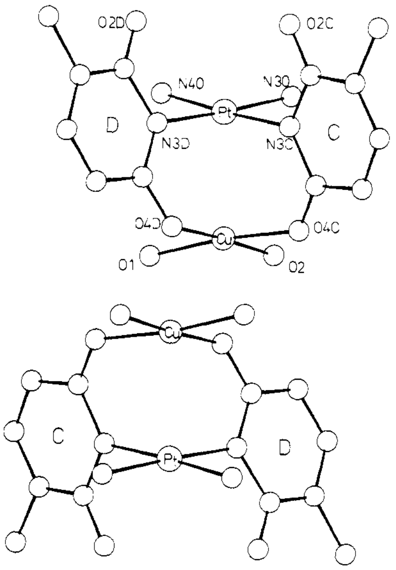

Figure 2. Pair of centrosymmetrically related cations of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(H_2O)_2]SO_4{\cdot}4.5H_2O$.

Table VIII. Conformational Parameters of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(H_2O)_2]SO_4{\cdot}4.5H_2O$[a]

(a) Dihedral Angles (Deg)			
(N30, N40, N3D, N3C)/ring 1	91.7		
(N30, N40, N3D, N3C)/ring 2	111.8		
ring 1/ring 2	91.6		
(O1, O2, O4C, O4D)/ring 1	73.7		
(O1, O2, O4C, O4D)/ring 2	88.9		
(N30, N40, N3D, N3C)/(O1, O2, O4C, O4D)	25.8		
(b) Deviations of Pt and Cu from Their Coordination Planes (Å)			
ΔPt	+0.039	ΔCu	+0.070
(c) Deviations of Pt and Cu from Least-Squares Planes of Rings C and D (Å)			
ΔPt(ring C)	0.022	ΔCu(ring C)	0.477
ΔPt(ring D)	0.068	ΔCu(ring D)	0.476

[a] Equations for planes: Pt coordination plane, $-0.9036X - 0.4198Y - 0.0846Z = -2.1884$; Cu coordination plane, $0.6877X + 0.7019Y - 0.1854Z = 5.0872$; Ring C, $0.4158X - 0.8731Y - 0.2544Z = -1.0247$; Ring D, $-0.3635X + 0.0844Y - 0.9277Z = -0.8065$.

hydrogen-bonding interactions are given in Table VII and conformational parameters in Table VIII. Because of the relatively large errors, no interatomic distances and angles of the 1-MeU rings are listed.

Each cation consists of a Pt,Cu dimer with two 1-MeU ligands in head–head arrangement, bridging through N3 (Pt) and O4 (Cu). The first coordination sphere of Pt is completed by two NH_3 ligands in cis positions to each other and that of Cu by two H_2O ligands cis as well. Pt–N bond lengths are normal (cf. preceding section) and so are Cu–OH_2 distances.[31] Bond angles around Cu and Pt are close to 90° as expected for square-planar coordination. Within a dimer Pt and Cu are separated 2.765 (3) Å from each other. The two metals lie slightly out of the best planes through their coordinating atoms in a way that they approach each other: Pt, 0.039 Å; Cu, 0.070 Å. The coordination planes of both metals are slightly tilted toward each other (25.8°) as required by the N3,O4 bite distance and as observed in related complexes of 1-methylthymine,[8,13,15] 1-methyluracil,[9,19] and α-pyridone.[32] The 1-MeU ligands are planar within the standard deviations. Pt slightly deviates from the 1-MeU planes (−0.022 (A), +0.069 Å (B)), Cu markedly (−0.477 (A), −0.476 Å (B)). This, together with the IR data, which indicate a covalent Cu–O4 bond, implies a substantial deviation of O4 from sp^2 hybridization in the neutral 1-methyluracil toward sp^3 in the anionic ligand in **4**. Forced by the square-planar coordination spheres of both metals, the 1-MeU ligands are almost perpendicular to each other. The same holds for the above-mentioned Pt_2,[13] Pt_2,Mn,[15] and Pt_4,Ag[9] complexes, whereas in the Pt_2,Ag complex[14] with its distorted-tetrahedral coordination sphere of Ag, both ligands are tilted away from perpendicular positions relative to the Pt coordination planes and to each other.

Adjacent cations are related by a center of symmetry, leading to Cu–Cu* separations of 3.483 (5) Å. This distance certainly is too long to imply any significant Cu–Cu interaction. Also, Cu–O1* (4.036 (19) Å) and Cu–O2* (5.097 (22) Å) distances do not suggest any additional Cu–oxygen interaction, and the distance between aquo ligands of adjacent Pt,Cu dimers are well over 4 Å and therefore too long for any hydrogen bonding between these groups. There is, however, strong hydrogen bonding between the aquo ligands of Cu(II) and the disordered sulfate oxygens (2.61 (5)–2.71 (5) Å), but the sulfates do not link centrosymmetrically related cations as those shown in Figure 2 but Pt,Cu cations related by other symmetry operations. In addition, hydrogen bonding involving the noncoordinating oxygens of the 1-MeU ligands and water of crystallization and NH_3 ligands of neighboring cations, respectively, is possible.

^1H NMR Spectrum of *cis*-$Pt(NH_3)_2(1\text{-}MeU)_2$. ^1H NMR resonance of **1** and**2**, respectively, in D_2O (pD 7, 0.05 M Pt) are observed at 7.304 (H6), 5.516 (H5), and 3.264 ppm (N–CH_3)). All resonance are shifted upfield relative to those of neutral 1-methyluracil (7.596, 5.782, 3.358 ppm), very similar to the case for the bis(1-methylthyminato) complex of cis Pt(II)[16] and the bis(uridine) complex of $enPt^{II}$.[33] H5 and H6 resonances are coupled (7.3 Hz)8 and H5 exhibits additional ^{195}Pt–^1H coupling (15.1 Hz) as expected for N3 platinum binding.[11] There is no indication of additional signal splitting at 30 °C that could be attributed to the existence of stable stereoisomers with a high barrier of rotation, as observed with the bis(guanosine) complex of (*N,N,N′,N′*-tetramethylethylenediamine)platinum(II).[34,35] The formation of the head–head dimer **4** clearly proves that rotation of the 1-MeU ligands in solution is possible. As compared with those in bis(1-methylcytosine)[22] and bis(guanosine) complexes,[34] where unfavorable interligand interactions (missing hydrogen bonding, repulsion between identical exocyclic groups) do not stabilize a head–head arrangement of the two ligands in cis positions, the mutual repulsions of the exocyclic oxygens in the bis(1-methyluracil) complex should be comparable for the head–tail and head–head arrangements.

IR Spectra. A comparison of the IR spectra (Nujol) of the heteronuclear Pt,Cu complexes **4**–**8** reveals, apart from the anion vibrations, only very small differences. Such differences are to be seen in the OH stretching region and in the low-frequency region around 300 cm^{-1}, e.g. 315 s, b, 290 m, sh (**4**); 320 s, b (**5**); 320 s, 300 m (**7**); 328 s, 298 s cm^{-1} (**6**). The 1-MeU ligand modes between 1700 and 350 cm^{-1} virtually do not vary with the anion or the stoichiometry and therefore do not permit any differentiation between 1:1 and 2:1 complexes. On the other hand, Cu coordination to the (1-MeU) ligand is evident from a comparison of the IR spectra of *cis*-$Pt(NH_3)_2(1\text{-}MeU)_2$ (**1**, **2**) and the heteronuclear Pt,Cu complexes. This is to be seen most clearly in the double-bond stretching region with the shifts of these bands to lower energy on Cu binding: 1700 sh, 1660 sh, 1640 vs, 1568 vs, 1548 vs (**1**, **2**); 1660 sh, 1640 vs, 1535 vs cm^{-1} (**4**–**8**). Two other prominent shifts of intense 1-MeU modes on additional Cu binding refer to those at 600 and 495 cm^{-1} in **1** and **2**, which appear in

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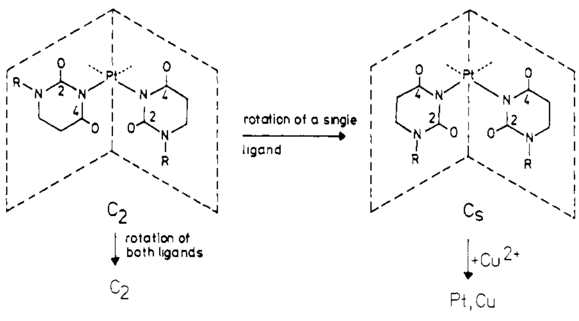
(35) It is noted that in the case of the bis(guanosine) complex signal splitting is attributed to a hindered interconversion of the two diastereomers (head–tail arrangement of ligands).

Scheme I



the Pt,Cu complexes at 625 and 510, 480 cm^{-1}. As expected, the IR spectra of the $NaNO_3$ adducts, with the exception of the NO_3^- absorptions, are identifical with those of **1** and **2**.

Discussion

The Pt,Cu and Pt,Na complexes described here represent other examples for the high tendency of N3 platinated pyrimidine-2,4-diones to bind additional cations through their exocyclic oxygen atoms. Although the X-ray structure of the Pt_2,Cu complex(es) has not been determined, it seems reasonable to assume a structure analogous to that of the Pt_2,Mn complex of 1-methylthymine with square-planar coordination geometries for all three metals.[15] Formation of **4** and **5** (SO_4^{2-} salts) is a consequence of the Pt:Cu ratio applied during the preparation, favoring **4** with high Cu:Pt ratios and **5** with an excess of Pt. No other products besides **4** and **5** were detected, not even with a fourfold excess of Cu over Pt. With $Cu(NO_3)_2$ instead of $CuSO_4$, only a single crystalline species was isolated (Pt_2,Cu), regardless whether the Cu:Pt ratio was 1 or 4. This suggests that the 1:1 complex is much more soluble than the obtained 2:1 compound. Similarly, the low solubilities of the Pt_2,Cu chloride and tetrachloroplatinate(II) probably account for the fact that with these anions only a single compound was isolated. With acetate as counterion always mixtures of Pt_2,Cu and Pt,Cu complexes were obtained but no separation in analytically pure materials could be achieved as with the sulfates **4** and **5**.

Formation of the N3,O4-bridged Pt,Cu complex **4** requires rotation of one of the two 1-MeU ligands of **1** (**2**) about the Pt–N3 bond. Despite the possibility of Cu coordination through one O2 and one O4, which would not involve a ligand rotation, twofold N3,O4 bridging apparently is more favorable than mixed (N3,O2), (N3,O4) bridging (Scheme I). The most plausible explanation for this finding is that O4 is more basic than O2. N3,O4 bridging has also been confirmed unambiguously in the head–tail dimer *cis*-$[Pt(NH_3)_2(1\text{-}MeU)]_2(NO_3)_2$[8] and in the pentanuclear complex *cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_4Ag(NO_3)_5$.[9] In the latter, in addition to N3,O4 Pt binding, also O2 binding to Ag is found. Several more examples of di- and trinuclear complexes of 1-methylthymine with assumed N3,O4 bridging exist.[13-15,19,20]

Our present data do allow us to draw some tentative conclusions concerning feasible stoichiometries and structures of heteronuclear complexes containing the *cis*-$Pt(NH_3)_2(1\text{-}MeU)_2$ or *cis*-$Pt(NH_3)_2(1\text{-}MeT)_2$ moiety and a heterometal M that is capable of assuming square-planar or tetrahedral coordination geometries. The main difference between tetrahedral and square-planar coordination of M is that Pt and M approach each other more closely in the case of square-planar coordination. The coordination geometry of the first heterometal M to react with the $(1\text{-}MeU)_2$ complex is governing the coordination geometry of any other metal M′ that binds to the Pt,M complex. For example, in the Pt_4,Ag compound, Ag is forced into a square-planar coordination geometry as a consequence of the same coordination sphere of Pt binding to O4. On the other hand, the separation of the free 1-MeT oxygens in the Pt_2,Ag complex[14] of about 3.4 Å is too large for a square-planar-coordinated metal but sufficient if binding of another metal occurred in a tetrahedral fashion.

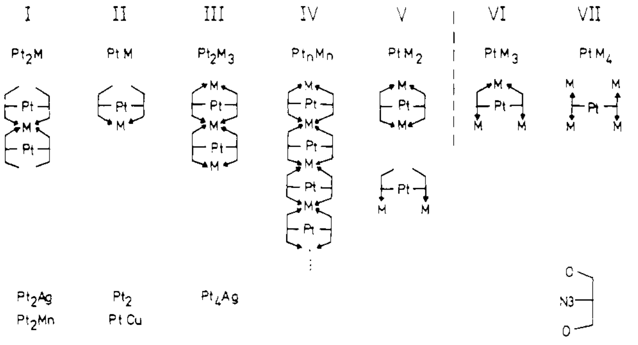


Figure 3. Feasible stoichiometries of heteronuclear complexes of *cis*-$Pt(NH_3)_2(1\text{-}MeU)_2$ and *cis*-$Pt(NH_3)_2(1\text{-}MeT)_2$, respectively.

As shown in Figure 3, a variety of stoichiometries can be envisaged and have, in part, been proven so far. Terminal M may be substituted by *cis*-$Pt(NH_3)_2^{2+}$ as seen with the head–head dimer of (1-MeT) or with the Pt_4,Ag compound of 1-MeU. The Pt_nM_n structure (IV in Figure 3), though not proven crystallographically for cis Pt(II) complexes yet, has some precedence in the Ag(1-MeT) complex described by Guay and Beauchamp.[17] It seems possible that the compound *cis*-$Pt(NH_3)_2(1\text{-}MeT)_2 \cdot AgNO_3 \cdot 4H_2O$, previously prepared by us,[14] crystallizes in this fashion, since it is of very low solubility as compared with that of similar dinuclear complexes. Structures VI and VII probably are unrealistic because of the expected increasing repulsion of three or four positively charged M's at two ligands. With the possibility of additional bridge formation of coordinating anions through terminal M's, the number of feasible stoichiometries further increases.

Acknowledgment. This study has been supported by the Deutsche Forschungsgemeinschaft, DFG, and the Technische Universität München. We thank J. Riede for his assistance, Dr. J. O. Besenhard for taking the X-ray powder patterns, and Professor T. J. Kistenmacher for discussions.

Registry No. 2, 83350-96-3; **4**, 83378-75-0; *cis*-$Pt(NH_3)_2(1\text{-}MeU)_2$, 83350-97-4; *cis*-$Pt(NH_3)_2(1\text{-}MeU)_2 \cdot 0.5NaNO_3$, 83350-98-5; *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(1\text{-}MeU)_2Pt(NH_3)_2]SO_4$, 83351-00-2; *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(1\text{-}MeU)_2Pt(NH_3)_2](NO_3)_2$, 83434-36-0; *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(1\text{-}MeU)_2Pt(NH_3)_2]Cl_2$, 83434-37-1; *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(1\text{-}MeU)_2Pt(NH_3)_2]PtCl_4$, 83434-38-2; *cis*-$[Pt(NH_3)_2(H_2O)_2](NO_3)_2$, 52241-26-6.

Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms of **2** and **4**, calculated and observed structure factor amplitudes for **2** and **4**, and distances and angles of the 1-MeV ligands of **4** (35 pages). Ordering information is given on any current masthead page.