where t is the pulse interval required for a null signal.

For each compound measured, the observed spectral width was chosen to be the narrowest which would encompass all the signals from the compound. For the progressive saturation method, the length for each measurement was 8192 points, the maximum available. This led to the digital resolution varying from 0.08 Hz/point to 1.25 Hz/point (for $Ru(S_2PMe_2)(PPh_2OEt)_2$). A sensitivity-enhancement weighting function was applied to all FID's before transformation, ensuring that sufficient points defined all peaks to be measured. Whenever possible, peak integrals were used. Analysis of the results was done by the classical semilog linearization followed by least-squares analysis of the straight line obtained. Comparison with the three-parameter nonlinear least-squares method of Gerhards[9] showed identical trends, with slight numerical differences in T_1 values.

For the inversion recovery method, a sweep width of 3012 Hz was used incorporating 4096 data points. An acquisition time/scan of 1.36 s was used and recovery times were chosen that were a minimum of 5 times the T_1 values. Delay times were set and data acquisition was performed by the computer T_1 program. Analysis of the data from T_1 measurements was by least-squares fitting of the semilog plot ln $(S_\infty - S_t)$ against t, whence the slope provides the T_1 value (S_∞ = equilibrium signal intensity, S_t = signal intensity at time t). A minimum of four time t values were used, and up to 1000 scans had to be collected to obtain acceptable signal-to-noise ratios in the signals. For each method we estimate our values to be good to ±6%.

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Registry No. $Ph_2PH(O)$, 4559-70-0; $Na[S_2PMe_2]$, 34669-04-0; $[NH_4][S_2PPh_2]$, 56152-33-1; $Ru(S_2PMe_2)[(OPPh_2)_3H_2]$, 79466-66-3; $PtH(PPh_2Me)[(OPPh_2)_2H]$, 68547-04-6; $(MeO)_2PH(O)$, 868-85-9; $PtCl(PEt_3)[(OP(OMe)_2)_2H]$, 63264-38-0; $Pt[(OP(OMe)_2)_4H_2]$, 30053-63-5; *cis*-$[Ru(S_2PMe_2)_2(PPh_2OEt)_2]$, 79547-84-5; *cis*-$[Ru(S_2PMe_2)_2(PPh_2H)_2]$, 79482-69-2; *cis*-$[Ru(S_2PMe_2)_2(PPhCl_2)_2]$, 79482-70-5; *cis*-$[Ru(S_2PMe_2)_2(PCl_3)_2]$, 79482-71-6.

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A Heteronuclear (Pt_4,Ag) Complex of 1-Methyluracil and Its Conversion into a Crystalline Platinum Blue

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Metal binding to the N3 position of the 1-methylthymine or 1-methyluracil monoanion (deprotonated at N3) facilitates binding of additional metals or of a proton through exocyclic oxygens of these ligands. This has been demonstrated for di-[1-3] and heteronuclear (Ag,[4] Mn,[5] H[6]) complexes of *cis*-$Pt(NH_3)_2^{2+}$ and a complex of Ag.[7]

We herewith report the synthesis and structure of another heteronuclear complex of 1-methyluracil containing four *cis*-$Pt(NH_3)_2^{2+}$ moieties and one Ag^+, $Ag[Pt(NH_3)_2(1\text{-}MeU)]_4(NO_3)_5{\cdot}4H_2O$ (**1**),[8] and its conversion into a crystalline "platinum blue" of composition $[Pt(NH_3)_2(1\text{-}MeU)]_4(NO_3)_5{\cdot}5H_2O$ (**2**). Although the insufficient crystal size of **2** so far has prevented the X-ray structure determination,[9] there is considerable evidence (vide infra) that it is the analogue of the "α-pyridone blue".[10]

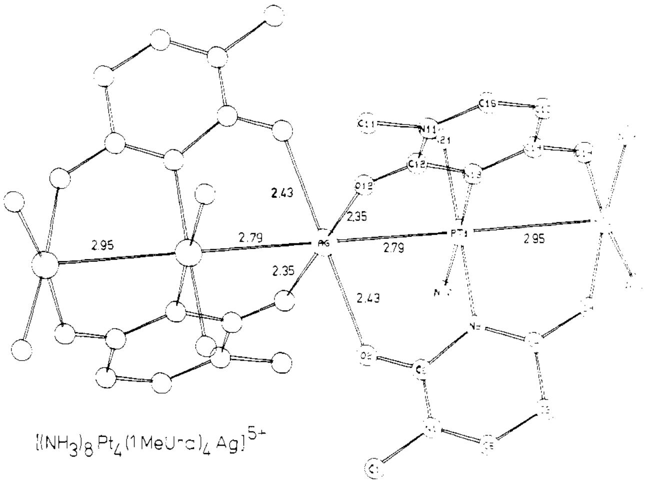

Figure 1. Molecular cation of **1**, $[(NH_3)_4Pt_2(C_5H_5N_2O_2)_2Ag(C_5H_5N_2O_2)_2Pt_2(NH_3)_4]^{5+}$.

Crystals of **1** were isolated from a solution of the head-to-head dimer *cis*-$[Pt_2(NH_3)_4(C_5H_5N_2O_2)_2](NO_3)_2{\cdot}H_2O$[11] (425 mg in 15 mL of H_2O), to which $AgNO_3$ (338 mg) had been added, upon slow evaporation (pH 4–5). The yield was 100 mg of **1** within 1–2 days; deep yellow crystals, somewhat photosensitive (gradual darkening on exposure to light). Characterization was accomplished by X-ray analysis[12] and elemental analysis.[13] Among other products, that will be reported on later, varying amounts (5–30 mg) of a second crystalline compound **2** were isolated. The identical compound **2** was also obtained when **1** was dissolved in water (O_2 free, saturated with N_2) and kept in a sealed tube. The color of the solution (0.1 M Ag, pH 2–3) rapidly changed from yellow immediately after being dissolved to turquois or, if briefly (5–15 min) warmed to 80 °C, to blue.[14] Formation of the blue color was observed regardless of whether the sample was exposed to daylight or not. Upon cooling, crystals of **2** precipitated from the blue solution along with other products.[15] Separation was accomplished by hand under a microscope, and recrystallization was from water. With the warmed sample, occasional formation of a metallic mirror (Ag) was observed, wheras with samples kept at 3–22 °C, formation of some black

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(8) 1-MeU is the monoanion of 1-methyluracil.

(9) Crystal size ca. 1 × 0.02 × 0.02 mm.

(10) (a) Barton, J. K.; Rabinowitz, H. N.; Szalda, D. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 2827. (b) Barton, J. K.; Szalda, D. J.; Rabinowitz, H. N.; Waszczak, J. V.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 1434.

(11) Preparation analogous to that of the corresponding 1-methylthymine dimer (ref 1). Elemental analysis was satisfactory for C, H, N, and Pt.

(12) The crystal data of **1** are a = 14.418 (3) Å, b = 12.894 (4) Å, c = 13.527 (3) Å, β = 99.86 (2)°, V = 2477.6 Å^3, space group $P2_1/c$, Z = 2, ρ_{calcd} = 2.55 g cm^{-3}, and ρ_{obsd} = 2.53 g cm^{-3}. The 2566 observed reflections (Syntex $P2_1$ diffractometer, λ = 0.71069 Å, 2° ≤ 2θ ≤ 48°, $F_o > 4.7\sigma_{F_o}$, empirical absorption correction) gave a final $R = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.072. The structure was solved by MULTAN 80 and difference Fourier syntheses. The heavy atoms were refined anisotropically and all light atoms, except the hydrogens, isotropically. One of the anions is positioned at a center of inversion and is disordered.

(13) Anal. Calcd for $AgPt_4C_{20}H_{48}N_{21}O_{27}$: C, 12.62; H, 2.55; N, 15.46; Ag, 5.67. Found: C, 12.52; H, 2.72; N, 15.04; Ag, 5.58.

(14) With diluted samples, formation of an olive green color was observed on heating.

(15) Other identified products were: $[Pt_2(NH_3)_2(1\text{-}MeU)_2](NO_3)_2$ (head-to-head dimer) and $Pt(NH_3)_2(1\text{-}MeU)_2{\cdot}0.5AgNO_3$. No attempts were made to optimize the yield of **2**.

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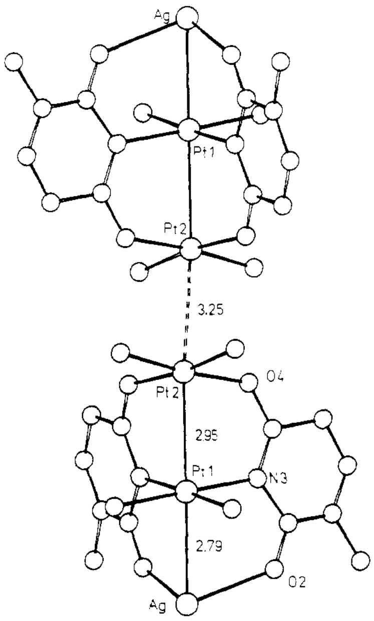


Figure 2. Arrangement of adjacent cations of **1** (only Pt_2Ag shown), related by a crystallographic inversion center in the middle of the intermolecular (3.25 Å) Pt–Pt vector.

precipitate was observed along with **2** and the other products.[15] Elemental analysis of **2** fits the above formulation as a mixed-valence oxidation state platinum compound (average 2.25);[16] dichroic columns (reddish brown in transparent light across the short axes, blue-black across the long axis), which dissolve with blue-green color in water and can be recrystallized from it without appreciable loss. A Nujol mull is greenish black and a KBr disk, purple.[17] Potentiometric titration of **2** with CuCl in 1 N HCl at 50 °C[18] (in HCl **2** becomes yellow) gave a sharp jump in voltage after addition of exactly 1 equiv of CuCl per 4 equiv of Pt, thus agreeing with a Pt_4^{9+} oxidation state. EPR measurements of **2**, performed at 22 °C with a polycrystalline sample, gave two principal g values ($g_\perp$ = 2.458, $g_\parallel$ = 1.992) with no indication of any hyperfine splitting as previously observed with powder samples of "platinum pyrimidine blues" at room temperature.[19,20]

The cation of the heteronuclear Pt_4,Ag complex is shown in Figure 1. Characteristic structural features of **1** are as follows: The molecular cation shows crystallographic centrosymmetry with Ag being in the inversion center. Ag therefore has a square-planar coordination with four O2 oxygens of 1-methyluracil ligands, two of each platinum dimer. Within each dimer, two *cis*-$Pt(NH_3)_2^{2+}$ moieties are bridged by 1-methyluracilato ligands in head-to-head arrangement, with Pt bound to N3 and O4, respectively. Thus each 1-MeU ligand simultaneously binds to three metal centers, two Pt, and one Ag.

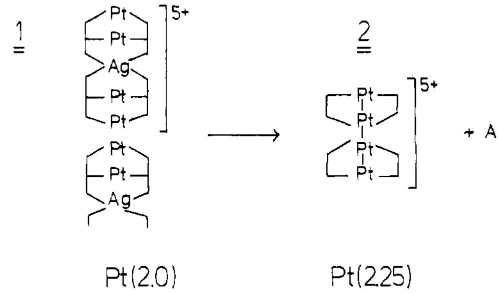
Adjacent cations are related by another inversion center, leading to a molecular structure with stacks of Pt_4 units interrupted by Ag (Figure 2). The Pt–Pt distance within a dimer is 2.949 (2) Å, the Pt–Pt distance between adjacent dimers is 3.246 (2) Å. Pt coordination planes within a dimer are tilted toward each other by an angle of 31.5°, very similar to the other dimers reported so far.[1-3,21] The Pt_4 unit thus has structural features ressembling those of the Pt^{II}–α-pyridone dimer-of-dimers,[21] although both intra- and interplatinum bond distances are somewhat longer in the here described compound. The Pt–Pt distance within each dimer of **1** is also somewhat longer than in the head-to-head platinum dimer of 1-methylthymine.[1] This probably is a consequence of the additional binding of Ag to 1-MeU in our heteronuclear complex. The Pt–Ag distance of 2.787 (1) Å is shorter than that in the earlier reported Pt_2,Ag complex of 1-methylthymine (2.849 (1) Å[4] and must be due to the square-planar coordination of Ag in **1** which allows a closer approach of the two metals as compared to the tetrahedral coordination of Ag in the Pt_2,Ag compound.

Table I. Structural Parameters of **1**, the α-Pyridone Pt(II) Dimer-of-Dimer,[21] the α-Pyridone Blue,[10] and the Head-to-Tail (1-MeU)Pt^{II} Dimer[3]

		α-pyridone		
	1	dimer-of-dimer	blue	1-MeU dimer
Pt–Pt_{intra}, Å	2.949 (2)	2.88	2.77	2.954 (2)
Pt–Pt_{inter}, Å	3.246 (2)	3.13	2.88	5.10
Pt–NH_3(av), Å	2.05 (2)	2.05	2.06	2.05 (2)
Pt–N(av), Å	2.08 (2)	2.05	2.05	2.05 (2)
Pt–O(av), Å	2.09 (2)	2.04	2.04	2.05 (2)
Ag–O, Å	2.43 (2), 2.35 (2)			
Pt–Ag, Å	2.787 (1)			
τ,[a] deg	31.5	30	27.4	35.8
ω,[b] deg	4.5	21	22	17-21

[a] Tilting angle between adjacent Pt coordination planes.
[b] Rotation of the Pt coordination planes about the Pt(1)–Pt(2) vector within a Pt_2 dimer.

In Table I structural parameters of the Pt_4,Ag complex **1**, the α-pyridone dimer-of-dimers,[21] the α-pyridone blue,[10] and the 1-methyluracil head-to-tail dimer[3] are compared. The molecular structure of **1** by itself offers a rationale for the formation of **2**, suggesting the following redox reaction:



Even though the oxidative potential of the Ag^+/Ag^0 couple is not high enough to enable a complete oxidation of Pt_4^{8+} to Pt_4^{9+}, it is sufficient to produce measurable quantities of **2**. Formation of metallic silver during the conversion **1** → **2** certainly supports the above formulation, as do reductive titration and the EPR spectrum of **2**.

Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft, DFG, and the Technische Universität München. We thank J. Riede (X-ray work), R. Bruchhaus (EPR spectrum), and M. Gnann for experimental assistance.

Registry No. **1**, 79534-50-2; **2**, 79828-18-5; *cis*-$[Pt_2(NH_3)_4(C_5H_5N_2O_2)_2](NO_3)_2$, 79534-48-8.

Supplementary Material Available: A list of atomic coordinates (1 page). Ordering information is given on any current masthead page.

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[16] Anal. Calcd for $Pt_4C_{20}H_{54}N_{21}O_{28}$: C, 13.36; H, 3.03; N, 16.37; O, 24.93. Found: C, 13.29; H, 3.15; N, 16.15; O, 24.75. The compound does not contain Ag.

[17] IR bands (Nujol) in the double bond stretching region of **2** (1680 s, 1640 vs, 1585 s, 1524 vs, 1485 s cm^{-1}) differ considerably from those of **1** (1635 vs, 1615 s, 1520 vs, 1480 s cm^{-1}).

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[20] The fact that no hyperfine splitting is observed in the EPR spectrum of **2** at room temperature may be a consequence of the higher concentration of unpaired spins as compared to the samples mentioned in ref 19.

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