From Simple *trans*-[a_2Pt(2-hydroxypyrimidine)$_2$]$^{2+}$ (a = NH_3, CH_3NH_2) Complexes to Structures of Higher Complexity. Molecular Recognition of 2-Aminopyrimidine by Hydrogen Bond Formation and Reactivity toward Additional Metal Ions

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The new complexes *trans*-[a_2Pt(Hpymo-N^1)$_2$]X_2 (*a* = NH_3, X= NO_3 **(1a)**; a = CH_3NH_2, X= NO_3 **(1b)**; a = CH_3NH_2, X= ClO_4 (**1c**); Hpymo = 2-hydroxypyrimidine) have been prepared by reaction of *trans*-[a_2Pt(H_2O)$_2$]X_2 with 2-hydroxypyrimidine at 80 °C in water. Complex **1c** cocrystallizes in water with 2-aminopyrimidine (ampym) through formation of complementary pairs of hydrogen bonds to give the supramolecular hexagon {*trans*-[(CH_3NH_2)$_2$Pt(pymo-N^1)(Hpymo-N^1)]·Hampym}$_2$(ClO_4)$_4$ (**2**). Molecular recognition of ampym by **1c** is responsible for a conformational change of the two hydroxypyrimidine ligands in **1c** from anti (**1c**) to syn and in addition for a proton transfer from a Hpymo residue to ampym against 1.5 units of pK_a gradient. ^{1}H NMR concentration-dependent studies as well as NOE experiments in dmso-d_6 and dmf-d_7 show that **2** dissociates in solution. Compound **1a** reacts in NH_3:H_2O (1:3) with Ag^I to give the polymeric species {*trans*-[(NH_3)$_2$Pt(μ-pymo-N^1,N^3)$_2$Ag(H_2O)]NO_3}$_n$ (**3**). In contrast to **2**, in the polymeric structure the *trans*-[(NH_3)$_2$Pt(pymo)$_2$] entities adopt an anti conformation. Nevertheless, the [(H_2O)Ag(pymo)$_2$] residues present a syn conformation that leads to a meander-like global structure. Compounds **1b**, **1c**, **2**, and **3** have been studied by X-ray crystallography: **(1b)** triclinic space group, $P\bar{1}$, a = 9.300(2) Å, b = 10.483(2) Å, c = 11.050(2) Å, α = 68.21(3)°, β = 75.47(3)°, γ = 73.83(3)°, Z = 2, R1 = 0.025, and wR2 = 0.062; **(1c)** triclinic space group, $P\bar{1}$, a = 5.692(1) Å, b = 7.758(2) Å, c = 11.236(2) Å, α = 93.12(3)°, β = 92.86(3)°, γ = 102.58(3)°, Z = 2, R1 = 0.048, and wR2 = 0.119; (**2**) triclinic space group, $P\bar{1}$, a = 8.355(2) Å, b = 11.221(2) Å, c = 13.004(3) Å, α = 86.76(3)°, β = 78.62(3)°, γ = 77.96(3)°, Z = 2, R1 = 0.033, and wR2 = 0.080; **(3)** monoclinic space group, $C2/c$, a = 5.345(1) Å, b = 23.998(5) Å, c = 12.474(2) Å, β = 102.27(3)°, Z = 8, R1 = 0.041, and wR2 = 0.093.

Introduction

Hydrogen bonding is a design principle in supramolecular chemistry[1] and crystal engineering.[2] Another strategy for the construction of supramolecular materials is the use of the coordinative bond. This alternative has also received great attention because of the interest in polymeric structures containing transition metals which possess the magnetic, optical, catalytic, and structural properties intrinsic of the metal ions.[3] The simultaneous use of hydrogen bond formation and metal coordination combines the two approaches and has led to a wealth of structural features.[4]

Our interest in this field—combining coordination chemistry and H bonding—stems from our efforts to model metal−nucleobase interactions in an attempt to better understand the possible effects of metal ions for nucleobase pairing and the role of metal ions in stabilizing larger nucleobases entities.[5] Among others, this has led us to formally replace weakly acidic protons in H bonds between nucleobases by metal ions of suitable geometry to generate metal-modified base pairs,[6] triplets,[7] quartets[8] hexagons,[9] and self-assembled nucleobase aggregates,[10] including a molecular box.[9,11] The relevance of these compounds ranges from biology (possible role of metal ions in nucleobases mispairing and mutagenesis) to molecular

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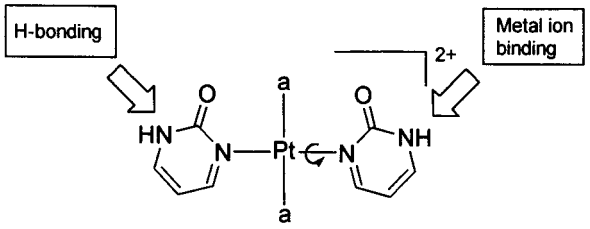
Scheme 1



biology (possible use of metalated oligonucleotides in antisense and antigene strategies[12]) and host−guest chemistry.[13]

The use of *trans*-a_2Pt^{II} (a = NH_3, CH_3NH_2) in this study has proven to be particularly useful. Here, we report on complexes derived from this metal entity and the 2-hydroxypyrimidine ligand (Hpymo) and demonstrate how the simple compound *trans*-$[a_2Pt(Hpymo)_2]X_2$ (X = NO_3, ClO_4) can be used to generate structures of higher complexity by taking advantage of its H bonding and metal binding properties, respectively (Scheme 1).

Experimental Section

Materials. *trans*-$(NH_3)_2PtCl_2$[14a] and *trans*-$(CH_3NH_2)_2PtCl_2$[14b] were prepared from K_2PtCl_4. 2-Hydroxypyrimidine·HCl (Hpymo·HCl) and 2-aminopyrimidine (ampym) were purchased from Aldrich. 2-Hydroxypyrimidine·HCl was converted to the corresponding HNO_3 adduct by anion exchange. **Caution!** Perchlorate salts are potentially explosive and should be used in small quantities.

Preparation of *trans*-$[(NH_3)_2Pt(Hpymo)_2](NO_3)_2$ (1a). *trans*-$(NH_3)_2PtCl_2$ (1.5 mmol) was added to an aqueous solution of $AgNO_3$ (3 mmol in 50 mL of H_2O) and the suspension was stirred in the dark at 40 °C for 22 h. The resulting mixture was kept at 4 °C for 2 h before the AgCl precipitate was filtered off. Subsequent addition of a solution of Hpymo·HNO_3 (3 mmol in 27 mL of H_2O) resulted in the formation of a white turbid solution (pH 1.9). After the pH was raised to 3.1 by means of 2 N NaOH, the mixture was reacted at 80 °C for 2 h. Filtration of a small amount of undissolved material afforded a pale yellow solution which was concentrated to 8 mL. After 2 weeks, a white powder was recovered. The product was washed with a small amount of water and air-dried. The yield was 476 mg (44%). Anal. Calcd for $PtC_8H_{14}N_8O_8$: C, 17.60; H, 2.59; N, 20.53. Found: C, 17.2; H, 2.6; N, 20.4.

Preparation of *trans*-$[(CH_3NH_2)_2Pt(Hpymo)_2](NO_3)_2$ (1b). A procedure analogous to **1a** was applied with *trans*-$(CH_3NH_2)_2PtCl_2$ used instead of *trans*-$(NH_3)_2PtCl_2$. In this case, the concentration of the reaction solution to 8 mL afforded, after 2 h, colorless X-ray quality crystals of **1b**. The yield was 488 mg (57%). Anal. Calcd for $PtC_{10}H_{18}N_8O_8$: C, 20.95; H, 3.16; N, 19.54. Found: C, 21.0; H, 3.1; N, 19.7.

Preparation of *trans*-$[(CH_3NH_2)_2Pt(Hpymo)_2](ClO_4)_2$ (1c). The compound was obtained following the addition of $NaClO_4$ (120 mg in 1 mL of H_2O) to a concentrated aqueous solution of **1b** (0.5 mmol of **1b** in 2 mL of H_2O). After 2 h, colorless crystals of **1c** were obtained; the yield was 170 mg (52%). Anal. Calcd for $PtCl_2C_{10}H_{18}N_6O_{10}$: C, 18.53; H, 2.80; N, 12.97. Found: C, 18.5; H, 2.8; N, 13.2.

Preparation of *trans*-$[(CH_3NH_2)_2Pt(Hpymo)(pymo)](ClO_4)_2$·(Hampym) (2). A 4-fold excess of ampym (0.62 mmol in 1 mL of H_2O) was added to a solution of **1c** (0.15 mmol in 2 mL of H_2O). The resulting colorless solution (pH 4.8) afforded crystals of **2** within 24 h at room temperature. The crystals were filtered and dried in air. The yield was 33 mg (29%). Anal. Calcd for $PtCl_2C_{14}H_{23}N_9O_{10}$: C, 22.62; H, 3.12; N, 16.96. Found: C, 22.6; H, 3.0; N, 17.0.

Preparation of *trans*-$[(NH_3)_2Pt(pymo)_2Ag(H_2O)]NO_3$ (3). Two solutions containing $AgNO_3$ (0.37 mmol in 2 mL of NH_3:H_2O (1:3)) and **1a** (0.18 mmol in 10 mL of NH_3:H_2O (1:3)) were mixed. The colorless solution was left for 24 h at room temperature to afford an abundant amount of crystals of **3**. The product was filtered and dried in air; the yield was 84 mg (77%). Anal. Calcd for $AgPtC_8H_{14}N_7O_6$: C, 15.82; H, 2.32; N, 16.15. Found: C, 15.8; H, 2.3; N, 16.1.

Instruments. IR spectra (KBr pellets) were recorded on a Bruker IFs 113v FT spectrometer. The ^1H NMR experiments were recorded in D_2O with sodium-3-(trimethylsilyl)-1-propanesulfonate (TSP) as the internal reference and in dmso-d_6 and dmf-d_7 with TMS as the internal reference, on Bruker DRX 400 and Bruker AC 200 instruments.

Solution Studies. Acidity constants in D_2O (pK_{a/D_2O}) of 2-Hpymo, 2-ampym, and **1a** were determined by evaluating the change in the chemical shifts of the H3, H5, and H6 protons of 2-hydroxypyrimidine and 2-aminopyrimidine residues, dependent on the adjusted p*D* values (DNO_3/NaOD). All experiments were performed at 5 mM concentration of the respective species, at 20 °C. The changes in the chemical shifts were evaluated by a Newton-Gauss nonlinear least-squares curve-fitting procedure. The relationship between the observed chemical shift and the varying p*D* values is described by eq 1, which was derived analogous to ref 15:

$$\delta_{obs} = \frac{\delta_L + \delta_{HL} \times 10^{(pK_{a/D_2O} - pD)}}{1 + 10^{(pK_{a/D_2O} - pD)}} \quad (1)$$

In eq 1 δ_{HL} and δ_L represent the chemical shifts of the pyrimidine derivatives which can be protonated (LH) or deprotonated (L) at the N1 and N3 positions. pK_{a/D_2O} corresponds to the negative logarithm of the acidity constant. This acidity constant, which describes the situation in D_2O, can be transformed to aqueous solution (H_2O) by application of eq 2:[16]

$$pK_{D_2O} = (1.015 \times pK_{H_2O}) + 0.45 \quad (2)$$

Crystallography. Intensity data for **1b**, **1c**, **2**, and **3** were collected on an Enraf-Nonius-KappaCCD[17] (graphite monochromator) with sample-to-detector distances of 30.2, 29.2, 29.2, and 28.7 mm, respectively. They covered the whole sphere of reciprocal space by measurement of 360 frames rotating about ω in steps of 1° with scan times of 15 s (**1b**, **1c**) and 10 s (**2**, **3**) per frame. Preliminary orientation matrixes and unit cell parameters were obtained from the peaks of the first 10 frames, respectively, and refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO.[18] The scaling as well as the global refinement of crystal parameters were performed by SCALEPACK.[18] Reflections, which were partly measured on previous and the following frames, were used to scale these frames on each other. This procedure in part eliminates absorption effects and also considers a crystal decay if present.

The structures were solved by standard Patterson methods[19] and refined by full-matrix least-squares based on F^2 using the SHELXTL-PLUS[20] and SHELXL-93 programs.[21] The scattering factors for the atoms were those given in the SHELXTL-PLUS program. Transmission factors were calculated with SHELXL-97.[22] All non-hydrogen atoms

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Table 1. Crystallographic Data for **1**, **2**, **3**, and **4**

	1	**2**	**3**	**4**
empirical formula	$C_{10}H_{21}N_8O_{9.5}Pt$	$C_5H_{91}N_3O_5ClPt_{0.5}$	$C_{14}H_{23}N_9O_{10}Cl_2Pt$	$C_4H_7N_{3.5}O_3Ag_{0.5}Pt_{0.5}$
fw	600.44	324.15	743.40	303.61
temp, K	163(2)	293(2)	163(2)	163(2)
λ, Å	0.71069	0.71069	0.71069	0.71069
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a, Å	9.300(2)	5.692(1)	8.355(2)	5.345(1)
b, Å	10.483(2)	7.758(2)	11.221(2)	23.998(5)
c, Å	11.050(2)	11.236(2)	13.004(3)	12.474(2)
α, deg	68.21(3)	93.12(3)	86.76(3)	
β, deg	75.47(3)	92.86(3)	78.62(3)	102.27(3)
γ, deg	73.83(3)	102.58(3)	77.96(3)	
V, Å^3	947.5(3)	482.6(2)	1168.7(4)	1563.5(5)
Z	2	2	2	8
ρ_{calc}, g cm^{-3}	2.105	2.231	2.112	2.580
μ(Mo Kα), mm^{-1}	7.471	7.610	6.303	10.232
T_{min}, T_{max}	0.1179, 0.1635	0.0865, 0.2163	0.1980, 0.3018	0.0798, 0.1927
R1[a]	0.0253	0.0480	0.0328	0.0410
wR2[b]	0.0623	0.1189	0.0800	0.0930
max Fourier diff, e Å^{-3}	1.282	2.302 (close to Pt)	1.318	1.809 (close to Pt)

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. ^{1}H NMR (200 MHz) Data in ppm (and Coupling Constants in Hz) for Compounds **1a**, **1b**, and **2** in D_2O and dmso-d_6 at 295 K[a]

	Hpymo				ampym			$MeNH_2$	
compounds	H3	H4	H5	H6	H4, H6	H5	NH_2	Me	NH_2
1a (D_2O, pH* 3)		8.34 ($J_{4,5}$ = 6.2, $J_{4,6}$ = 2.5)	6.85 (J = 5.9)	9.04 ($J_{5,6}$ = 5.7, $J_{4,6}$ = 2.5, $J_{Pt,H}$ = 43.8)					
1b (D_2O, pH* 3)		8.39 ($J_{4,5}$ = 6.2, $J_{4,6}$ = 2.5)	6.89 (J = 5.9)	9.19 ($J_{5,6}$ = 5.7, $J_{4,6}$ = 2.5, $J_{Pt,H}$ = 46.5)				2.21 (J = 12.8, $J_{Pt,H}$ = 38.6)	
1b (dmso-d_6)	13.4	8.38 ($J_{4,5}$ = 5.9, $J_{4,6}$ = 2.6)	6.69 (J = 5.9)	8.90 ($J_{5,6}$ = 5.5, $J_{4,6}$ = 2.4)				2.06 (J = 5.9)	5.00 (J = 5.7)
2 (D_2O, pH* 3)		8.38	6.86	9.19 (J = 2.0)	8.38	6.86		2.21 (J = 3.1)	
2 (dmso-d_6)	13.4	8.38 ($J_{4,5}$ = 5.9.2, $J_{4,6}$ = 2.6)	6.69 (J = 5.9)	8.90 ($J_{5,6}$ = 5.5, $J_{4,6}$ = 2.4)	8.21 (J = 4.8)	6.55 (J = 4.8)	6.63	2.06 (J = 5.9)	5.00 (J = 5.7)

[a] Asterisk at pH denotes uncorrected pH meter reading.

were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined with a common isotropic temperature factor, except for those in **2**, which could be localized with difference Fourier synthesis and were fully refined. None of the structures showed any disorder besides the perchlorate anion in **1c**, where three of the oxygens were spread over six positions.

Crystal data and data collection parameters are summarized in Table 1.

Results and Discussion

Solution Studies of *trans*-[a$_2$Pt(Hpymo-*N*^{1})$_2$]X$_2$. The new complexes *trans*-[a$_2$Pt(Hpymo-*N*^{1})$_2$]X$_2$ (*a* = NH_3, X= NO_3 (**1a**); a = CH_3NH_2, X= NO_3 (**1b**); a = CH_3NH_2, X = ClO_4 (**1c**)) have been prepared by reaction of *trans*-[a$_2$Pt(H_2O)$_2$]X$_2$ and Hpymo at 80 °C in water. ^{1}H NMR spectra of complexes **1a**−**1c** are diagnostic of the coordination mode (Table 2). They show the loss of the original equivalence of the H4 and H6 protons in Hpymo and the shift of the H4 (−0.03 ppm), H5 (+0.14 ppm), and H6 (+0.72 ppm) resonances of the pyrimidine ring after Pt coordination to N1. At the same time, observation of ^{195}Pt satellites at the H6 resonances ($J_{Pt,H} \approx 45$ Hz) clearly indicates that Pt coordination occurs at N1. The observation of only one set of signals for each resonance of the pyrimidine ring agrees with fast rotation (on the NMR time scale) about the Pt−N1 bond (see below). pH*-dependent ^{1}H NMR studies indicate a significant acidification of the Hpymo residues after Pt binding (pK_2 = 8.7 ± 0.2 for free Hpymo and pK_a = 5.39 ± 0.09 for **1a**). In the deprotonation process of **1a** only one step is observed, indicating that the first ($Pt(LH)_2^{2+} \rightarrow PtL(LH)^+ + H^+$) and the second ($PtL(LH)^+ \rightarrow PtL_2 + H^+$) deprotonation step overlap. For this reason the approximation (eq 1, Experimental Section) was used which considers a single pK_a value only rather than two for the 2:1 complex. Assuming two mutually unaffected deprotonation steps, theoretical values of p$K_1 \approx 5.1$ and p$K_2 \approx 5.7$ can be estimated for the two processes.[23] The basicity of the exocyclic O2 atom of the Hpymo ligand appears to be very low. Thus, there is no sign from ^{1}H NMR spectroscopy for protonation of the Hpymo ligands, at O2, in compounds **1a**−**1c** down to pH* 0, and we have no evidence of heterometal ion binding to this site. In this aspect Hpymo differs from the related uracil and thymine heterocycles for which an increased basicity of the exocyclic oxygens is found after Pt binding, as expressed by ready protonation and metal binding.[24]

Crystal Structures of 1b and 1c. Suitable crystals for X-ray crystallography were obtained for **1b** and **1c**. The crystals contain *trans*-[$(CH_3NH_2)_2$Pt(Hpymo-*N*^{1})$_2$]$^{2+}$ cations, nitrate (**1b**)

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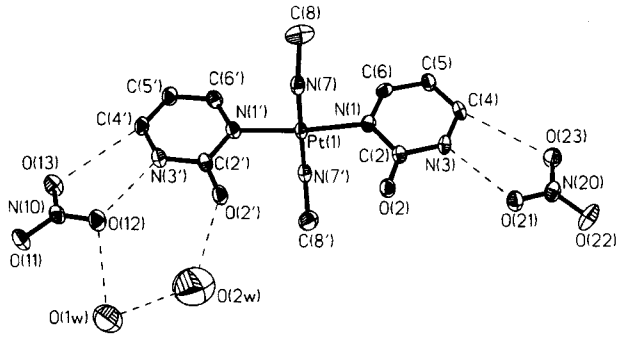

Figure 1. View of the molecular structure of complex **1b**. Ellipsoids are drawn at the 50% probability level.

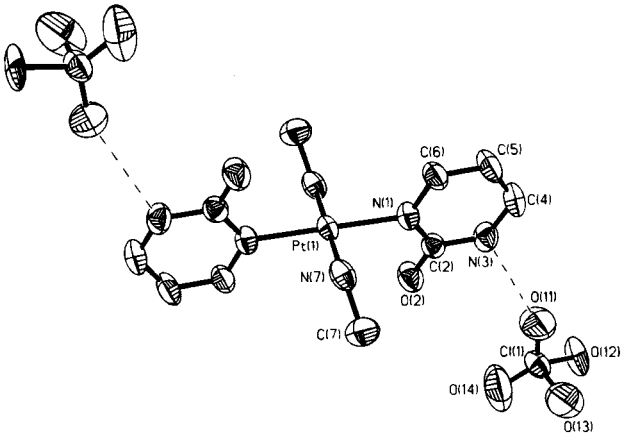

Figure 2. View of the molecular structure of complex **1c**. Pt1 is located at a crystallographic symmetry center. Ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Distances (Å), Angles (deg), and H-Bonding Distances (Å) in the Crystal Structures of **1b**, **1c**, **2**, and **3**

	1b	**1c**	**2**	**3**
Pt−N1	2.014(4)	2.037(8)	2.019(5)	2.022(6)
Pt−N1′	2.025(4)	2.037(8)[a]	2.034(5)	2.022(6)[b]
Ag−N3				2.181(6)
Ag−O1				2.60(1)
N1−Pt−N1′	172.5(1)	180[a]	176.7(2)	180[b]
N7···O2		2.93(1)[c]		2.859(9)[d]
				2.86(1)[b]
N7′···O2	2.875(5)[e]		2.763(8)[e]	
N7′···O2′	2.872(6)[e]		2.914(7)[e]	
N1a···N3			2.803(8)[f]	
N2a···O2			2.820(8)[f]	
N3′···N3a			2.902(7)	
N2a···O2′			2.976(7)	

[a−f] Symmetry relations: [a] $-x, -y, -z$. [b] $0.5 - x, 0.5 - y, -z$. [c] $1 + x, y, z$. [d] $0.5 + x, 0.5 - y, 0.5 + z$. [e] $-x, 1 - y, 1 - z$. [f] $-1 - x, 1 - y, 1 - z$.

and perchlorate (**1c**) anions, and lattice water molecules (**1b**). Views of the molecular structures of compounds **1b** and **1c** are depicted in Figures 1 and 2, respectively. A selection of structural parameters for compounds **1b** and **1c** is listed in Table 3. As expected, Pt binding occurs for both compounds at the N1 donor atom of the pyrimidine ring. Bond distances within the Hpymo ligand are similar to those present when it is free[25] or coordinated in neutral form,[26] with only random deviations being observed. It is interesting to note that whereas in compound **1b** the two Hpymo ligands adopt a syn conformation (head−head) in **1c** an anti disposition (head−tail) is found. The head−head orientation of the pyrimidine residues in **1b** is stabilized by two H bonds between the N7′ atom of the amine group and the exocyclic oxygen atoms of the Hpymo entities of a symmetry-related cation. This motif is common in the stabilization of head−head Pt complexes containing related heterocycles.[27] It leads to the formation of hydrogen-bonded cationic dimers (Figure 3). In the case of **1c** the head−tail orientation of the Hpymo residues leads to the formation of a one-dimensional polymer along the crystallographic *a* axis, supported by hydrogen bond interactions between the Hpymo exocyclic oxygen atom and the amine N7 atom (Figure 4). The fact that the presence of different anions in the solid state influences the respective orientation of the pyrimidine residues indicates the low-energy barrier between both conformers and agrees with a free rotation about the Pt−N1 bond in solution. Additional hydrogen-bonding interactions between the N3 protons of the Hpymo ligands and the oxygen atoms of the anions are found in both compounds. It is also interesting to note for **1b** the additional interactions of C4−H···O23 and C4′−H···O13 of 3.167(7) and 3.087(7) Å, respectively (Figure 1). Similar interactions have been found for protonated cytosine model nucleobases containing ClO_4^- and NO_3^- anions.[28]

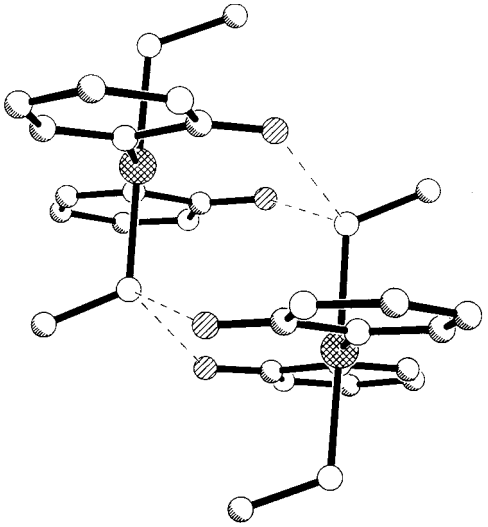

Figure 3. Association of cations *trans*-$[(CH_3NH_2)_2Pt(Hpymo\text{-}N^1)_2]^{2+}$ as dimers in **1b** as a result of hydrogen-bonding interactions between the exocyclic O2 atom of the Hpymo and the amine groups bound to Pt.

Molecular Recognition of 2-Aminopyrimidine by 1c. The mutual orientation of the N3−H donor sites and the O2 acceptor sites in **1b** led us to pursue the idea that H-bonding schemes with suitable complementary molecules could generate cyclic or polymeric entities. To this end we have cocrystallized **1c** with an excess of 2-aminopyrimidine (ampym) in water (pH 4.8) and obtained crystals of composition {*trans*-$[(CH_3NH_2)_2$-

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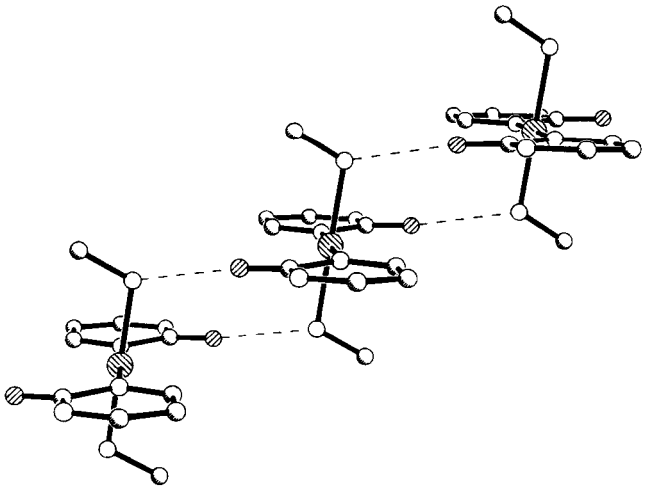


Figure 4. View of the cationic chains $\{trans\text{-}[(CH_3NH_2)_2Pt(Hpymo\text{-}N^1)_2]\}_n^{2n+}$ in **1c** formed by the hydrogen-bonding interactions between the exocyclic O2 atom of Hpymo and the amine groups of neighboring $trans\text{-}[(CH_3NH_2)_2Pt(Hpymo\text{-}N^1)_2]^{2+}$ entities.

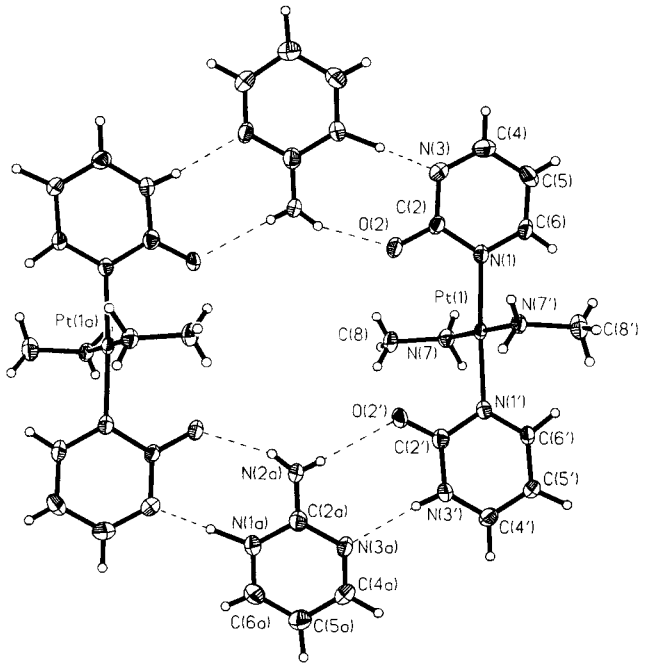
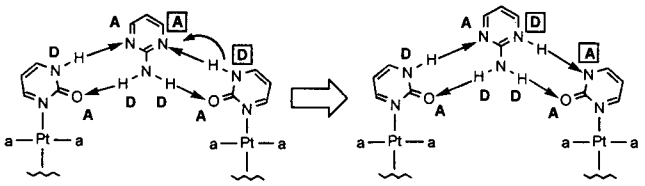


Figure 5. View of the supramolecular structure of compound **2**. The hydrogen atoms were found in the Fourier-difference map; the perchlorate anions are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

$Pt(Hpymo\text{-}N^1)_2]\cdot ampym\}(ClO_4)_2$ (**2**), which confirmed such a possibility. A view of the supramolecular structure of **2** is shown in Figure 5. In Table 3, a selection of structural parameters is given. The crystals consist of $trans\text{-}[(CH_3NH_2)_2Pt(pymo\text{-}N^1)(Hpymo\text{-}N^1)]^+$, monoprotonated ampym cations ($Hampym^+$), and perchlorate anions. The solution of the X-ray structure revealed that molecular recognition of ampym through pairs of complementary hydrogen bonds takes place and leads to the self-assembly of two $trans\text{-}[(CH_3NH_2)_2Pt(Hpymo\text{-}N^1)_2]^{2+}$ entities and two ampyms to give the supramolecular hexagon $\{trans\text{-}[(CH_3NH_2)_2Pt(pymo\text{-}N^1)(Hpymo\text{-}N^1)]\cdot Hampym\}_2^{4+}$ (**2**). A similar molecular recognition process between uracil and 2,4,6-triaminepyrimidine has been previously employed to assemble a bisporphyrin supramolecular cage.[29] Molecular recognition of ampym by **1c** is responsible for an anti to syn conformational change of the $trans\text{-}[(CH_3NH_2)_2Pt(Hpymo\text{-}N^1)_2]^{2+}$ entities.

Scheme 2



Moreover, the quality of the crystals permitted us to locate the hydrogen atoms. X-ray analysis revealed that a proton transfer from a Hpymo residue to ampym against 1.5 units of pK_a gradient has taken place ($pK_2 = 3.57 \pm 0.05$ for ampym vs $pK_1 \approx 5.1$ for **1c**). This process appears to be favored on one hand by a more even charge distribution along the cyclic supramolecular cation (four +1 charged cations rather than two +2 charged cations plus two neutral molecules), and on the other hand because this proton transfer results in the formation of a particularly favorable H-bonding scheme in **2** (Scheme 2): Thus, instead of two pairs of DA:AD hydrogen bonds (I), H^+ transfer from Hpymo to ampym generates in addition to the DA:AD pair a pair of DD:AA type bonds (II) which is energetically favored over the former.[30,31] The different hydrogen-bonding patterns result in a marked difference in the interatomic distances (compare N3′···N3a of 2.902(7) and N2a···O2′ of 2.976(7) Å versus N2a···O2 of 2.820(8) and N1a···N3 of 2.803-(8) Å). This proton transfer is also responsible for the loss of the original equivalence of both sides of the ampym derivative which results in a situation analogous to the known "Janus wedges", which are able to mediate H-bonding interactions between nucleobases after their insertion.[32] Examination of internal bond angles of the pyrimidine ligands bound to Pt provides additional proof that N3 is deprotonated. The angle C2−N3−C4 in **2** closes by 5° as compared to that in **1c**. Similarly, for 2-aminopyrimidine the angle C2a−N1a−C6a opens by 2.6° as a consequence of protonation at N1a as compared to the angle C2a−N3a−C4a.

The packing of the structure reveals a stairlike arrangement of the hexagons (Figure 6) in which the head−head disposition of the Hmtpo residues is additionally stabilized in an analogous way to **1b** by the formation of two hydrogen bonds between the N7′ atoms and the (H)pymo exocyclic oxygen atoms of the next step of the stair.

One-dimensional ^1H NMR concentration-dependent studies of **2** (dmso-d_6, 200 MHz, 293 K, (5×10^{-4})−0.1 M) do not show any effect of concentration on individual NH and NH_2 resonances. Likewise, NOE experiments in dmso-d_6 (400 MHz, 0.04 M, 293 K) and dmf-d_7 (400 MHz, 0.04 M, 263 K, 293 K) reveal that the cyclic structure of **2** is not retained in solution.

Reactivity of $trans\text{-}[a_2Pt(Hpymo\text{-}N^1)_2]X_2$ toward Metal Ions. The possibility of deprotonating the N3 positions of the two Hpymo ligands of **1** permits binding of additional metal ions to these sites. Thus, reaction of **1a** with Ag^I in water at pH > 3 resulted in the immediate precipitation of a white product of composition $trans\text{-}[(NH_3)_2Pt(pymo)_2Ag(H_2O)]NO_3$ (**3**). When the reaction was carried out in NH_3:H_2O (1:3), X-ray quality

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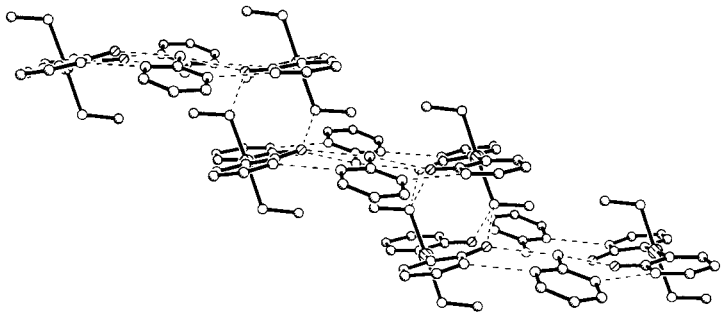


Figure 6. Association of the supramolecular hexagons of **2** in the solid state.

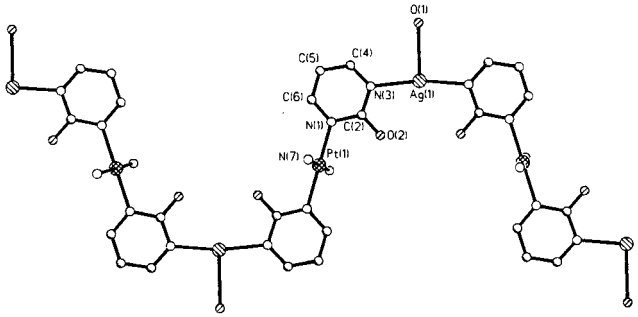


Figure 7. Section of the one-dimensional chain structure of **3.** The nitrate anions are omitted for the sake of clarity.

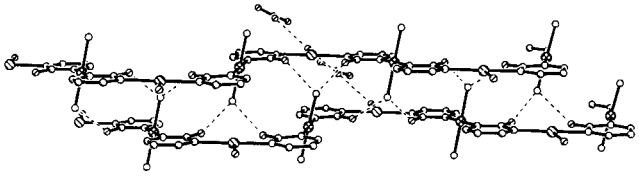
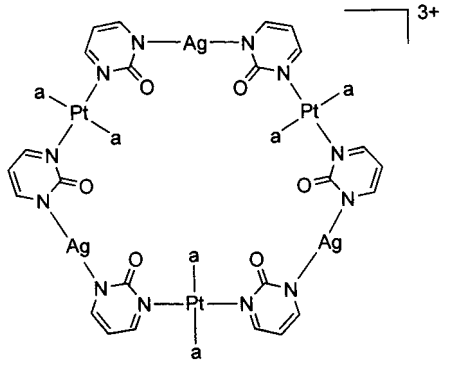


Figure 8. Association of chains of **3** by means of hydrogen-bonding interactions between the ammine groups bound to Pt and the O2 exocyclic atoms. Additional hydrogen-bonding interactions between the polymeric cations are mediated by the nitrate anions which in turn interact with the water molecules bound to Ag.

crystals were obtained. In addition, the reaction of **1a** and **1b** with *trans*-$[a_2Pt(H_2O)_2](NO_3)_2$ at pH 5−6 and 60−80 °C was also probed. However, although reaction at the N3 donor atom takes place according to one-dimensional ^{1}H NMR spectroscopy (200 MHz, 295 K, D_2O, pH* 4.8, 0.05 M), it was not possible to isolate a compound of defined structure. Reaction of **1a** with *trans*-$[(NH_3)_2Pt(D_2O)_2]^{2+}$ produces broad signals for H5 (6.6 ppm) and H4 (8.6 ppm) resonances of pymo in the ^{1}H NMR spectra and a broad signal at −2500 ppm in the ^{195}Pt NMR (D_2O, 313 K, pH* 4.8) spectrum. Analogously, reaction of **1b** with *trans*-$[(CH_3NH_2)_2Pt(D_2O)_2]^{2+}$ is responsible for broad signals for H5 (6.8 ppm) and H6 (8.8 ppm) resonances of pymo residues and a broad signal centered at −2600 ppm in the ^{195}Pt NMR (D_2O, 313 K, pH* 4.8, 0.05 M) spectrum. The shifts of the H5 and H4 resonances of pymo in the ^{1}H NMR spectra and of the ^{195}Pt NMR signal are in accord with metalation taking place at N3. Nevertheless, the broadness of the signals points to the possible formation of polymeric structures of random length. Attempts to separate defined species by chromatography were not successful.

X-ray Structure of *trans*-$[(NH_3)_2Pt(pymo\text{-}N^1,N^3)_2Ag(H_2O)]NO_3$ (3). Selected bond distances and angles for **3** are given in Table 3. A view of the polymeric compound is shown in Figure 7. The structure solution revealed the composition of the material as a polymeric cation of type $\{(NH_3)_2Pt(pymo\text{-}N^1,N^3)_2Ag(H_2O)\}_n^{n+}$ whose charge is neutralized by NO_3^- anions (see Figure 7). In the polymer the Pt atoms alternate with the Ag atoms. The *trans*-$(NH_3)_2Pt(pymo)_2$ entities of the starting compound **1a** are preserved. The Pt−N1 bond length is in the same range as those found for compounds **1b**, **1c,** and **2**. As in **1c**, the orientation of the pyrimidine ligands is head−tail. Ag coordination occurs as expected at the basic N3 donor atom, leading to the observed polymeric structure. This result is in accord with the previously observed tendency of the Ag/Hpymo[33,34] system and other nitrogen heterocycles to generate polymeric structures.[35] The Ag−N separation is in the same order as those found for the cyclic species $\{Ag(pymo\text{-}N^1,N^3)\}_6$[34] and the polymer $\{Ag(pymo\text{-}N^1,N^3)\}_n$.[33] Additionally, a water molecule is weakly bonded to the silver center, leading to a distorted trigonal−planar geometry about Ag. A similar coordination pattern has been previously observed in a mixed adenine, cytosine complex of Ag.[36] It is interesting to note that the pyrimidine residues in the $Ag(H_2O)(pymo)_2$ entities display a head−head orientation, which is again stabilized (see above) by H-bonding interactions with the amino groups bound to Pt of neighboring chains (see Figure 8). This results in an alternating head−tail orientation of the pyrimidine entities at the Pt centers and head−head orientation of the pyrimidine residues at the Ag centers, which gives rise to a meander-like overall structure. With respect to the geometry of the pyrimidine ligands it is only interesting to note that deprotonation of the N3 atom leads to a closing of the C2−N3−C4 angle by 6°, similar to the situation in **2**.

Scheme 3



Although not observed in the present case, the formation of a cyclic structure consisting of six metal ions ($3Pt^{II}$, $3Ag^{I}$) and six pymo ligands is feasible on steric grounds, provided the two pymo rings bound to each Pt adopt a head−head arrangement (Scheme 3). Whether or not a suitable template species

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could favor such a structure over a polymeric one remains to be seen.

Conclusions

By making use of the hydrogen-bonding possibilities of the simple *trans*-$[a_2Pt(Hpymo\text{-}N^1)_2]^{2+}$ complexes, it is possible to build structures of higher complexity through the formation of complementary hydrogen-bonding interactions with 2-aminopyrimidine. Interaction of the *trans*-$[a_2Pt(Hpymo\text{-}N^1)_2]^{2+}$ complexes with additional metal ions leads to the formation of polymeric structures after coordination of the new metal to the basic N3 donor atoms of the pyrimidine ring.

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Supporting Information Available: Tables listing atomic coordinates, temperature factors, bond lengths and angles, torsion angles, and details of refinement of the X-ray crystallographic data for compounds **1b**, **1c**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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