

Heavy Transition Metal Complexes of Biologically Important Molecules. 3. Crystal and Molecular Structure of Bis(μ -1-methylthyminato-*N*3,*O*4)bis-(*cis*-diammineplatinum(II)) Dinitrate Hydrate, $[(\text{NH}_3)_2\text{Pt}(\text{C}_6\text{H}_7\text{N}_2\text{O}_2)_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2\cdot\text{H}_2\text{O}$

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Abstract: The reaction of $(\text{NH}_3)_2\text{Pt}(\text{OH})_2\text{Pt}(\text{NH}_3)_2^{2+}$ with 1-methylthymine yields the novel compound bis(μ -1-methylthyminato-*N*3,*O*4)bis(*cis*-diammineplatinum(II)) dinitrate hydrate, $[(\text{NH}_3)_2\text{Pt}(\text{C}_6\text{H}_7\text{N}_2\text{O}_2)_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2\cdot\text{H}_2\text{O}$. The crystal structure has been determined by x-ray diffraction. The monoclinic space group $P2_1/c$ has cell dimensions $a = 8.394$ (4), $b = 18.271$ (9), $c = 17.279$ (7) Å, $\beta = 116.77$ (3)° and has four formula units in the unit cell. Data were collected using Mo K α radiation and a Syntex P2₁ diffractometer. The crystal structure was determined by standard methods and refined to $R_1 = 0.0546$, $R_2 = 0.0562$ based on 3642 independent reflections. The cation is a dimer in which the two square planar arrays about each platinum atom lie above each other, and these are bridged in *cis* positions by the 1-methylthyminato ligands through N3 and O4. The bridging ligands are arranged head to tail. The Pt–Pt distance (2.974 (1) Å) is short enough to suggest a metal–metal bond. Pt–N distances (range 2.014 (9)–2.064 (8) Å) and Pt–O distances (2.013 (7), 2.037 (7) Å) are normal. The relationship of the title compound to the platinum–pyrimidine blues is discussed.

Certain *cis*-diammineplatinum(II) complexes are useful anticancer agents² and it is postulated that the mechanism of action is complex formation between the *cis*-diammineplatinum(II) compound and the purine and pyrimidine bases of deoxyribonucleic acid (DNA). Many complexes have been suggested on the basis of solution studies, with complex formation between the ribose or alkyl-blocked base and platinum occurring at N3 for cytosine, N7 for guanine, and N1 and N7 for adenine.^{3,4} In addition chelate formation between either N7 and 6-NH₂ or N1–6-NH₂ was claimed for adenine. No evidence was obtained for strong complex formation with thymine or uracil. Many of these suggestions have been confirmed by the isolation of solid complexes which were examined by single-crystal x-ray diffraction. Thus, platinum coordination has been confirmed at the N3 position of cytosine,^{5,6} N1 and N7 positions of adenine,^{7,8} and the N7 position of guanine.^{9,10} In only one case has it been shown that two platinum atoms are attached to one base, namely, the N1 and N7 positions of adenine.⁸ In this case the platinum atoms are separated by a substantial distance and are clearly independent.

It is postulated, however, that reactions of compounds such as *cis*-PtCl₂(NH₃)₂ with the DNA bases and even with DNA itself *in vivo* go through an aquation product, supposedly $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{2+}$.¹¹ Recently we have shown that aqueous solutions of the aquation product are very complex and, in addition to such species as the above, may contain substantial amounts of hydroxide-bridged species containing two,¹² three,^{13,14} or four¹⁵ platinum atoms. One assumes that interaction of these species and the DNA bases will be more complex.

Recently Lippard et al.¹⁶ have prepared a "platinum blue" from α -pyridone units bridging the terminal pairs of platinum atoms. Lippard suggested that such binding may take place between pairs of platinum atoms and the N1–O6 positions of guanine. We have recently prepared the first direct reaction product of $[(\text{NH}_3)_2\text{Pt}(\text{OH})_2\text{Pt}(\text{NH}_3)_2]^{2+}$ and a DNA base, 1-methylthymine, and the complex bears some resemblance to Lippard's "blue." We describe this work here.

Experimental Section

Preparation of Bis(μ -1-methylthyminato-*N*3,*O*4)bis(*cis*-diammineplatinum(II)) Dinitrate Hydrate, $[(\text{NH}_3)_2\text{Pt}(\text{C}_6\text{H}_7\text{N}_2\text{O}_2)_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2\cdot\text{H}_2\text{O}$. *cis*-Pt(NH₃)₂Cl₂ (Matthey Bishop) was aquated by reaction with 99.5% of the stoichiometric amount of AgNO₃ in the dark, overnight, on a 0.1 M scale. An equimolar amount of 1-methylthymine (Heterocyclic Corp.) in H₂O was added. The pH was adjusted with NaOH to 6.5. After 1 week at 37 °C a dark blue solution formed (solution volume 100 mL). Absolute ethanol was added to give a total volume of 200 mL and a powdery blue precipitate formed leaving a yellow, supernatant solution. The blue solid was collected by filtration and the volume of the supernatant was reduced substantially. The precipitation with ethanol had to be repeated a number of times in order to remove all of the blue component. The final yellow solution was allowed to evaporate in the refrigerator to form yellow crystals of the product which were collected, washed with 95% ethanol, and dried in air. Anal. Calcd for C₁₂H₂₈N₁₀O₁₁Pt₂: C, 16.4; H, 3.2; N, 15.9; O, 20.0; Pt, 44.4. Found: C, 16.9; H, 3.3; N, 16.3.

Collection of the X-Ray Data. A crystal of the title compound, chosen after examination on a polarizing microscope, was ground to a cylinder of dimensions 0.35 mm length \times 0.08 mm radius.

Precession photographs of zero and first layers showed the crystal was monoclinic with systematic absences $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$, showing the unique space group $P2_1/c$ (no. 14). The crystal was transferred to a Syntex P2₁ diffractometer and mounted roughly along $[10 - 1]$. Accurate parameters were obtained from a least-squares fit of χ , ϕ , 2θ for 15 medium-angle ($20^\circ < 2\theta < 35^\circ$) reflections: $a = 8.398$ (4), $b = 18.271$ (9), $c = 17.279$ (7) Å, $\beta = 116.77$ (3)°. ($\lambda = 0.71069$ Å for Mo K α at 22 °C.) With $Z = 4$, ρ_{calcd} was 2.47 g cm⁻³ and ρ_{obsd} , determined by flotation in a methyl iodide/bromoform mixture, was 2.43 (5) g cm⁻³. The linear absorption coefficient was 125.1 cm⁻¹ and, using the above crystal dimensions, variation in the transmission coefficient was 4.61 to 5.06.

Intensities were measured using a P2₁ diffractometer and graphite monochromatized radiation for the quadrant $h, k, \pm l$ up to $2\theta = 55^\circ$. Data were collected using a coupled θ (crystal)– 2θ (counter) scan 1° on either side of the peak, scan rates varying from 2.02 to 29.3 deg min⁻¹ and being selected by the program supplied with the instrument.¹⁷ The stability of the instrument was monitored by measuring two standard reflections after every 14 reflections. The counting esd

Table I. Atom Parameters and Temperature Factors (\AA^2) ($\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Pt(1)	160.79 (6)	252.54 (2)	9.45 (3)	<i>a</i>
Pt(2)	33.10 (6)	235.81 (2)	143.51 (3)	<i>a</i>
N(1)	-23 (1)	54.9 (5)	-123.2 (6)	37 (2)
C(1)	5 (2)	18.6 (7)	-194.4 (9)	51 (3)
C(2)	77.7 (2)	115.2 (5)	-84.9 (7)	27 (2)
O(2)	192 (1)	137.9 (4)	-104.4 (5)	42 (2)
N(3)	35 (1)	152.3 (4)	-25.4 (5)	22 (2)
C(4)	-85 (2)	128.2 (5)	-3.5 (6)	28 (2)
O(4)	-108 (1)	155.9 (4)	57.8 (5)	36 (2)
C(5)	-198 (2)	67.1 (5)	-49.3 (7)	28 (2)
C(51)	-355 (2)	41.7 (7)	-32.6 (8)	46 (3)
C(6)	-160 (2)	33.0 (5)	-108.0 (7)	28 (2)
N(1A)	421 (1)	88.3 (5)	312.3 (6)	34 (2)
C(1A)	450 (2)	46.4 (8)	391 (1)	58 (4)
C(2A)	275 (2)	135.6 (5)	275.8 (6)	28 (2)
O(2A)	167 (1)	140.9 (5)	302.9 (6)	50 (2)
N(3A)	253 (1)	173.0 (4)	198.9 (5)	27 (2)
C(4A)	386 (1)	171.5 (5)	175.1 (6)	25 (2)
O(4A)	374 (1)	208.9 (4)	109.8 (4)	37 (2)
C(5A)	536 (2)	126.5 (6)	217.8 (7)	29 (2)
C(51A)	683 (2)	126.4 (7)	189.5 (8)	46 (3)
C(6A)	551 (2)	86.5 (6)	288.0 (8)	39 (3)
N(2)	-35 (1)	295.7 (5)	-102.8 (6)	40 (2)
N(4)	298 (1)	352.2 (5)	38.4 (7)	43 (3)
N(5)	170 (1)	316.5 (6)	230.6 (6)	43 (3)
N(6)	-194 (1)	298.6 (5)	93.4 (6)	38 (2)
N(7)	370 (2)	828.5 (6)	236.1 (7)	46 (3)
O(7)	232 (2)	818.6 (6)	244.7 (7)	77 (3)
O(8)	384 (2)	790.1 (7)	181.9 (7)	75 (3)
O(9)	480 (2)	876.0 (8)	276.1 (8)	89 (4)
N(8)	6 (2)	-15.3 (6)	407.5 (7)	45 (3)
O(10)	1 (2)	50.9 (6)	424.2 (7)	69 (3)
O(11)	-140 (1)	-46.4 (6)	361.2 (6)	60 (3)
O(12)	149 (2)	-45.6 (9)	434 (1)	109 (5)
O(13)	487 (2)	255.7 (5)	442.1 (7)	61 (3)

^a Anisotropic temperature factors U_{ij} were obtained from $\beta_{ij} = 2\pi^2 \mathbf{b}_i \mathbf{b}_j U_{ij}$ where β_{ij} 's occurs as a temperature effect of the form $\exp[-(\beta_1 h^2 + \dots + 2\beta_2 hk + \dots)]$ and \mathbf{b}_i and \mathbf{b}_j are the reciprocal lattice vectors. For Pt(1), $U_{11} = 274$ (4), $U_{22} = 205$ (2), $U_{33} = 287$ (2), $U_{12} = -12$ (2), $U_{13} = 136$ (2), $U_{23} = 13$ (1) and for Pt(2), $U_{11} = 248$ (4), $U_{22} = 241$ (2), $U_{33} = 283$ (2), $U_{12} = 28$ (2), $U_{13} = 139$ (2), $U_{23} = -24$ (1) (all $\times 10^4$).

of 2 - 1 - 6 was 3.0% with an overall esd of 6.5%; corresponding figures for 1 5 2 were 2.5 and 5.1%. The intensity of a reflection I , and its esd, $\sigma(I)$, were calculated as outlined previously;¹⁸ 4372 reflections were recorded, and after removing reflections which should be systematically absent and averaging, these were reduced to 3642 independent reflections, of which 2915 had $I > 3\sigma(I)$, 727 had $3\sigma(I) > I > \sigma(I)$, and 286 had $\sigma(I) > I$. These last were rejected. Corrections were made for absorption¹⁹ assuming that the crystal had the dimensions listed above. Unscaled structure amplitudes, F , and their standard deviations, $\sigma(F)$, were calculated from $F = (I/Lp)^{1/2}$, $\sigma(F) = 1/2(Lp)^{-1/2}(\sigma(I)^2/I)^{1/2}$. Lp , the Lorentz-polarization factor, was $(1 + \cos^2 \theta)/(2 \sin 2\theta)$.

Solution of the Structure. The platinum atoms were found from a three-dimensional Patterson synthesis and three-dimensional difference maps revealed the carbon, oxygen, and nitrogen atoms. Full-matrix least-squares refinement of these atom positions using anisotropic temperature factors for the platinum atoms and isotropic temperature factors for the light atoms and minimizing $W(|F_o| - |F_c|)^2$ proceeded smoothly and was terminated at $R_1 = 0.0546$, $R_2 = 0.0562$.²⁰ The weights used in the refinement were $\{\sigma(F)^2 + (0.03|F_o|)^2\}^{-1}$ and in the final cycle of refinement no parameter shifted by more than 0.19 of its esd. The error in an observation of unit weight was 1.22. Corrections were made for secondary extinction ($g = 1.21 \times 10^{-7}$).

The final difference map showed little variation, the highest peak being $0.91 \text{ e } \text{\AA}^{-3}$ at 0.22, 0.30, 0.01 near Pt(1) and the deepest valley being $-0.98 \text{ e } \text{\AA}^{-3}$ at 0.10, 0.19, 0.17 near Pt(1). Throughout the refinement the scattering curves used were taken from the Interna-

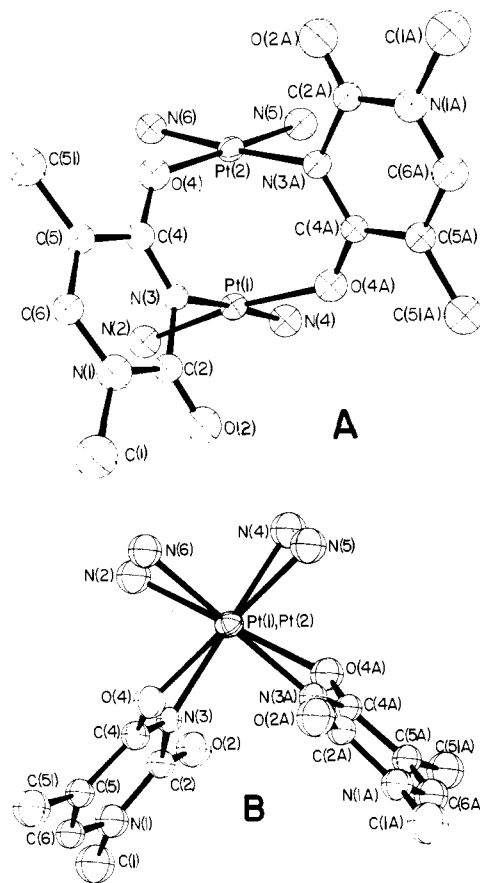


Figure 1. (A) The molecular cation $[(\text{NH}_3)_2\text{Pt}(\text{C}_6\text{H}_7\text{N}_2\text{O}_2)_2\text{Pt}(\text{NH}_3)_2]^{2+}$ with the platinum atoms in the plane of the paper, view distance ∞ . (B) The same cation viewed down the Pt(2)-Pt(1) vector, view distance ∞ .

tional Tables,²¹ and anomalous dispersion corrections from the International Tables²² were applied to the curve for platinum. The atom parameters for the nonhydrogen atoms are listed in Table I.

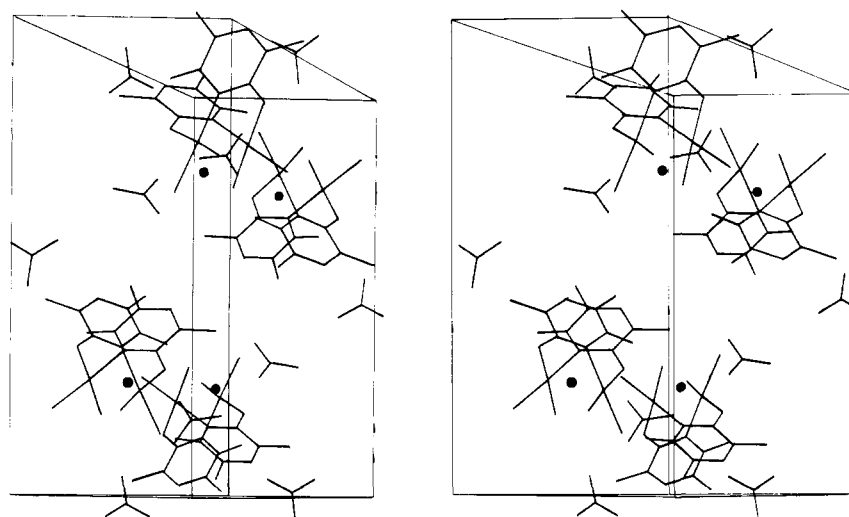
Results and Discussion

The molecular cation is shown in Figure 1 and selected interatomic distances and angles are given in Table II. The cation is dimeric, the two platinum atoms being bridged by the 1-methylthyminato ligands through N3 and O4. The two ammine groups are still cis on each platinum atom and the square planes of ligand atoms about each platinum lie roughly on top of each other. The N(3)-O(4) and N(3A)-O(4A) bite distances (2.25 (2), 2.29 (2) \AA) are considerably shorter than the Pt-Pt distance (2.974 (1) \AA) and this together with the square planar arrangement about each platinum atom causes the two platinum coordination planes to splay apart (dihedral angle 36.1°). This can be seen clearly in Figure 1A. In addition, the square planes are rotated by about 13-14.5° so that the atoms coordinated to one platinum atom do not lie directly above those on the other when viewed down the Pt-Pt vector (see Figure 1B). Thus the cation shows a strong resemblance to one half of Lippard's α -pyridone "blue" complex,¹⁶ although there are significant differences (see below). The Pt-N(H_3) (2.05 (1)-2.06 (1) \AA) distances do not differ significantly and are similar to previous values found by us^{12,13} and observed in Lippard's "blue".¹⁶ The Pt-N3²³ distances (2.014 (9), 2.064 (8) \AA) do differ significantly as do the Pt-O4 distances (2.013 (7), 2.037 (7) \AA) at the 95% confidence level. Both short distances are on the same ring (N3, O4). This means that each platinum atom has one long and one short distance to a 1-methylthyminato ligand. No significant differences in bond lengths or bond angles can be seen when comparing equivalent parameters in the 1-methylthyminato ligands and the values

Table II. Selected Interatomic Distances (Å) and Angles (deg)

Atoms	Distance	Atoms	Distance	Atoms	Distance
Pt(1)-Pt(2)	2.974(1)	Pt(1)-N(2)	2.054(9)	Pt(1)-N(4)	2.06(1)
Pt(1)-N(3)	2.064(8)	Pt(-O(4A))	2.013(7)	Pt(2)-N(5)	2.05(1)
Pt(2)-N(6)	2.05(1)	Pt(2)-N(3A)	2.014(9)	Pt(2)-O(4)	2.037(7)
N(3)-C(4)	1.30(2)	C(4)-O(4)	1.26(2)	C(4)-C(5)	1.45(1)
C(5)-C(51)	1.54(2)	C(5)-C(6)	1.35(2)	C(6)-N(1)	1.35(2)
N(1)-C(1)	1.51(2)	N(1)-C(2)	1.37(1)	C(2)-O(2)	1.22(2)
C(2)-N(3)	1.41(2)	N(3A)-C(4A)	1.35(2)	C(4A)-O(4A)	1.29(1)
C(4A)-C(5A)	1.41(2)	C(5A)-C(51A)	1.52(2)	C(5A)-C(6A)	1.37(2)
C(6A)-N(1A)	1.33(2)	N(1A)-C(1A)	1.48(2)	N(1A)-C(2A)	1.40(2)
C(2A)-O(2A)	1.20(2)	C(2A)-N(3A)	1.43(2)	N(7)-O(7)	1.24(2)
N(7)-O(8)	1.22(2)	N(7)-O(9)	1.23(2)	N(8)-O(10)	1.25(2)
N(8)-O(11)	1.26(1)	N(8)-O(12)	1.21(2)		
		Nonbonded Distances (Possible Hydrogen Bonds)			
N(2)-O(8)	3.05(2)	N(2)-O(7)	3.08(2)	N(2)-O(6)	3.06(2)
N(2)-O(10)	2.83(2)	N(4)-O(9)	2.94(2)	N(4)-O(10)	2.93(2)
N(4)-O(11)	3.16(2)	N(5)-O(9)	3.18(2)	N(5)-O(11)	2.91(2)
N(5)-O(2)	2.90(2)	N(6)-O(7)	2.98(2)	N(6)-O(12)	2.94(2)
N(6)-O(13)	2.95(2)	O(2)-O(13)	2.96(2)	O(2A)-N(2)	3.06(2)
O(13)-O(8)	2.87(2)				

Atoms	Angle	Atoms	Angle	Atoms	Angle
N(2)-Pt(1)-N(4)	89.9(4)	N(2)-Pt(1)-O(4A)	171.6(5)	N(2)-Pt(1)-N(3)	88.8(3)
N(2)-Pt(1)-Pt(2)	111.0(4)	N(3)-Pt(1)-N(4)	176.9(5)	N(3)-Pt(1)-O(4A)	92.3(3)
N(3)-Pt(1)-Pt(2)	79.6(3)	N(4)-Pt(1)-O(4A)	88.6(3)	N(4)-Pt(1)-Pt(2)	103.5(4)
O(4A)-Pt(1)-Pt(2)	77.4(3)	N(3A)-Pt(2)-N(5)	88.2(4)	N(3A)-Pt(2)-N(6)	176.6(5)
N(3A)-Pt(2)-O(4)	92.6(3)	N(3A)-Pt(2)-Pt(1)	81.6(3)	N(5)-Pt(2)-N(6)	90.9(4)
N(5)-Pt(2)-O(4)	178.6(5)	N(5)-Pt(2)-Pt(1)	102.5(4)	N(6)-Pt(2)-O(4)	88.2(3)
N(6)-Pt(2)-Pt(1)	101.8(3)	O(4)-Pt(2)-Pt(1)	78.7(3)	Pt(1)-N(3)-C(4)	125.1(8)
Pt(1)-N(3)-C(2)	112.0(8)	C(2)-N(3)-C(4)	122.5(9)	N(3)-C(4)-O(4)	123(1)
C(4)-O(4)-Pt(2)	129.5(8)	N(3)-C(4)-C(5)	120(1)	O(4)-C(4)-C(5)	117(1)
C(4)-C(5)-C(51)	122(1)	C(4)-C(5)-C(6)	117(1)	C(6)-C(5)-C(51)	121(1)
C(5)-C(6)-N(1)	121(1)	C(6)-N(1)-C(1)	119(1)	C(1)-N(1)-C(2)	117(1)
C(6)-N(1)-C(2)	123(1)	N(1)-C(2)-N(3)	116(1)	N(1)-C(2)-O(2)	122(1)
O(2)-C(2)-N(3)	122(1)	Pt(2)-N(3A)-C(2A)	114.8(9)	Pt(2)-N(3A)-C(4A)	124.9(7)
C(2A)-N(3A)-C(4A)	119.8(9)	N(3A)-C(4A)-C(5A)	121(1)	N(3A)-C(4A)-O(4A)	121(1)
C(4A)-O(4A)-Pt(1)	130.6(8)	O(4A)-C(4A)-C(5A)	118(1)	C(4A)-C(5A)-C(6A)	119(1)
C(4A)-C(5A)-C(51A)	120(1)	C(51A)-C(5A)-C(6A)	121(1)	C(5A)-C(6A)-N(1A)	120(1)
C(6A)-N(1A)-C(2A)	123(1)	C(6A)-N(1A)-C(1A)	117(1)	C(1A)-N(1A)-C(2A)	119(1)
N(1A)-C(2A)-N(3A)	116(1)	N(1A)-C(2A)-O(2A)	123(1)	O(2A)-C(2A)-N(3A)	121(1)
O(7)-N(7)-O(8)	115(1)	O(7)-N(7)-O(9)	123(1)	O(8)-N(7)-O(9)	122(2)
O(10)-N(8)-O(11)	117(1)	O(10)-N(8)-O(12)	119(1)	O(11)-N(8)-O(12)	124(1)

**Figure 2.** Stereogram (stereoscopic pair of perspective projections) of $[(\text{NH}_3)_2\text{Pt}(\text{C}_6\text{H}_7\text{N}_2\text{O}_2)_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. The contents of one cell, plus extra nitrate ions are shown. The water molecular is ●. **a** and **b** are parallel to the top and side of the page, respectively, and the view is down **c***.

reported here do not differ significantly from those for 1-methylthymine.²⁴ The platinum-platinum distance (2.974 (1) Å) is substantially longer than the equivalent distance in Lippard's compound (2.779 Å) as would be expected for Pt(II),

but nevertheless is much shorter than the values found for a bridging pyrophosphate complex (3.11 and 3.22 Å).²⁵ It is difficult to say whether this implies a metal-metal bond. The splaying apart of the square planes could be caused by plati-

num-platinum repulsion, but is more likely caused by the short bite distance of the pyrimidine ligands.

The formation of complexes of this type from the dimer can easily be understood since reaction of square planar Pt(II) complexes is postulated to go through a five-coordinate transition state. An incoming thymine group with N3 and O4 over the two platinum atoms in the dimer hydroxide will give five-coordinate platinum atoms at each end of the dimer, and will be in an ideal position to form the final product.

The packing within the unit cell is shown in Figure 2. The cations are arranged along the *c* direction such that there is a chain of platinum atoms at roughly $x = 0.1, y = 0.25$. Adjacent dimeric cations in the chain are related by the *c* glide. Thus there is a superficial resemblance to Lippard's blue. There are important differences, however. In Lippard's blue the platinum atom chain is only four atoms long because the ends are blocked with nitrate groups. In our compound the pyrimidine units in each dimer appear to be arranged head to tail. There is a possible ambiguity since N1 and C5 could be interchanged such that instead of bonding to the platinum atoms occurring through N3 and O4, the bonding is through N3 and O2. Statistical tests^{26,27} show that the model used here is correct at the 99.5% confidence level. Further preliminary structural studies on a similar complex of uracil, where there is no ambiguity, show bonding through N3 and O4.²⁸ The head to tail arrangement means that a ketone group protects each end of the dimeric cation and thus the platinum atoms in adjacent cations are a long distance apart (5.92 Å). This is in marked contrast to the 2.885 Å Pt-Pt interdimer distance observed in Lippard's blue, where the α -pyridone groups lie head to head and the ketone groups only protect one end of the dimeric unit.

Thus, the important difference in deciding whether the interaction of the bis- μ -hydroxo-bis(*cis*-diammineplatinum(II)) cation and pyrimidine bases can give rise to "blues" of the Lippard type appears to depend on whether the first dimeric product contains the pyrimidine bases in a head to tail arrangement, in which case no further reaction takes place, or a head to head arrangement, in which case a second dimerization and oxidation can give rise to a tetrameric blue. In addition, in the case of pyrimidine blues of this type, no further polymerization is likely to occur, since once a tetramer is formed both ends of the molecular cation will be protected by the pyrimidine groups (specifically O2 for 1-methylthymine and 1-methyluracil and 2-NH₂ for 1-methylcytosine).

For our compound the interactions holding dimeric units together within the chain are hydrogen bonds between O(2)-N(5) and O(2A)-N(5), and the water molecule lies between the cations lying roughly above O(4) (>3.4 Å), and hydrogen bonding to N(6) in the same molecular and O(2) in the adjacent molecule. In the *a* direction the chains are effectively separated by the N(7) nitrate ions which lie almost parallel to the N1-C2:N3-C4-C5-C6 1-methylthymine plane (dihedral angle 10.5°). In the *b* direction the N(8) nitrate groups lie between adjacent chains, but in addition there is contact between the ring methyl groups on adjacent chains. All contacts mentioned above are at or greater than the van der Waals contact distances.

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Supplementary Material Available: A table of moduli of the observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) (a) McMaster University; (b) Michigan State University.
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- (19) All calculations were carried out on a CDC-6400 computer. The programs DATCO3, ABSORB, and DATRDN from the X-RAY 71 package were used for preliminary data treatment. The full-matrix least-squares programs, CUDLS, Fourier program, SYMFOU, and least-squares planes program, PALS, were written locally by J. S. Stephens, J. S. Rutherford, and P. G. Ashmore, respectively. Diagrams were prepared using the program ORTEP by C. K. Johnson, U.S. Atomic Energy Commission Report, ORNL 3794, revised June 1955.
- (20) $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $R_2 = \{ \sum w |F_o| - |F_c| \}^2 / \sum w F_o^2 \}^{1/2}$.
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