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Crystal Structure of Bis(μ-1-methylthyminato-N3,O4)bis-(*cis*-diammineplatinum(II)) Dinitrate (Head–Head). Comparison with Related Compounds

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Abstract

The crystal structure of bis(μ-1-methylthyminato)-bis-(cis-diammineplatinum(II))dinitrate is reported. The compound crystallizes in space group $P2_1/n$ with $a = 8.424(2)$ Å, $b = 17.618(5)$ Å, $c = 15.861(2)$ Å, $\beta = 94.33(2)°$, $Z = 4$. The structure was refined on 3534 reflections to $R = 0.046$ and $R_w = 0.050$. The compound contains the 1-methylthyminato ligands, 1-MeT, in head–head arrangement with Pt binding through N3 and O4. Both Pt atoms have square-planar coordination spheres with the two coordination planes nearly eclipsed, yet tilted by an angle of 31.4°. The Pt–Pt distance within the cation is 2.927(1) Å, whereas the shortest intermolecular Pt–Pt separation is 5.66 Å. The crystal packing of this 1-MeT compound is different from that observed on related head–head dimers of cis-$(NH_3)_2Pt$.

Introduction

Dinuclear complexes of *cis*-$(NH_3)_2Pt$ containing two deprotonated cyclic amide ligands such as α-pyridone, α-pyrrolidone, 1-methylhydantoin, 1-methyluracil, and 1-methylthymine (Fig. 1) in head–head arrangement have aroused substantial interest because of their assumed role as precursors of 'platinum pyrimidine blues' [1]. With α-pyridone, for example, a close structural similarity between a pair of head–head dimers with Pt in its +2 oxidation state and a partially oxidized tetranuclear unit with an average +2.25 oxidation state for Pt has been demonstrated [2]. More recently, a tetranuclear α-pyrrolidone complex with an average Pt oxidation state of +2.5 has been shown to have a structure analogous to that of the α-pyridone blue [3]. These findings suggest that association of two head–head dimers is essential for the formation of partially oxidized species, at least if the heterocyclic ligand contains a single amidate group. With ligands containing additional functional groups as in the case of uracil or its derivatives, for example, other ways of producing extended Pt–Pt interactions seem to be possible as well. For this reason we have been interested in the crystal packing of related head–head dimers of *cis*-Pt(II) containing bridging 1-methyluracil [4] and 1-methylthymine ligands. In this paper we report the crystal structure of bis(μ-1-methylthyminato-N3,O4)bis-(*cis*-diammineplatinum-(II)) dinitrate which was previously described by us in preliminary form [5] and compare it with other head–head dimers of *cis*-diammineplatinum.

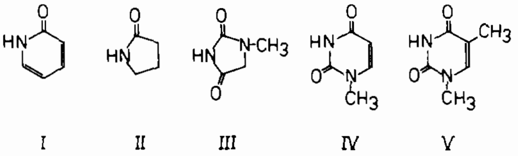

Fig. 1. Cyclic amide ligands with reported head–head arrangement in complexes of *cis*-$(NH_3)_2Pt$: α-pyridone, I, α-pyrrolidone, II, 1-methylhydantoin, III, 1-methyluracil, IV, and 1-methylthymine, V.

Experimental

The compound was prepared as previously described by reaction of *cis*-$(NH_3)_2Pt(1\text{-MeT})_2$ with *cis*-$[(NH_3)_2Pt(H_2O)_2](NO_3)_2$ [5]. A crystal fragment of dimensions 0.15, 0.15, 0.20 mm was used for the X-ray measurements which were carried out on a Philips PW 1100 instrument using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71069$ Å). The space group of the monoclinic crystal as determined from the systematic absences is $P2_1/n$. The cell parameters were determined by a least-squares fit of the parameters of the orientation matrix to the setting angles of 21 reflections. They are a = 8.424(2), b = 17.618(5), c = 15.861(2) Å, β =

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TABLE I. Atomic Parameters and Anisotropic Temperature Factors.*

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt1	0.0661(1)	0.5626(1)	0.2360(1)	0.021(1)	0.028(1)	0.023(1)	0.000(1)	−0.001(1)	−0.001(1)
Pt2	0.4076(1)	0.5635(1)	0.2862(1)	0.018(1)	0.036(1)	0.029(1)	−0.002(1)	0.000(1)	−0.000(1)
N11	0.0508(11)	0.6262(5)	0.1267(5)	0.047(6)	0.038(5)	0.033(5)	0.013(4)	−0.000(4)	0.001(4)
N12	0.0504(11)	0.4657(5)	0.1648(5)	0.053(6)	0.039(5)	0.024(4)	−0.001(4)	−0.004(4)	0.003(5)
N21	0.4827(10)	0.4657(5)	0.2343(6)	0.035(5)	0.039(5)	0.049(6)	−0.008(5)	0.002(4)	0.006(4)
N22	0.5096(10)	0.6239(5)	0.1951(5)	0.042(5)	0.044(5)	0.033(5)	0.005(4)	0.013(4)	−0.012(4)
N1a	−0.0818(11)	0.7614(5)	0.3561(6)	0.042(6)	0.033(5)	0.061(6)	−0.003(5)	0.012(5)	0.011(4)
C1a′	−0.2417(17)	0.7974(9)	0.3558(12)	0.053(9)	0.087(11)	0.134(15)	−0.013(11)	0.034(9)	0.042(8)
C2a	−0.0698(13)	0.6997(7)	0.3047(7)	0.037(6)	0.040(7)	0.046(6)	0.004(6)	0.002(5)	0.007(5)
O2a′	−0.1865(10)	0.6796(5)	0.2565(6)	0.022(4)	0.064(6)	0.088(7)	−0.008(5)	−0.017(4)	0.008(4)
N3a	0.0754(9)	0.6600(5)	0.3048(5)	0.020(4)	0.044(5)	0.029(4)	−0.005(4)	−0.009(3)	0.006(4)
C4a	0.2081(13)	0.6907(6)	0.3463(6)	0.040(6)	0.035(6)	0.028(5)	0.000(5)	0.009(5)	−0.000(5)
O4a′	0.3423(8)	0.6601(4)	0.3416(5)	0.025(4)	0.037(4)	0.053(5)	−0.020(4)	0.004(3)	−0.005(3)
C5a	0.1953(12)	0.7569(6)	0.3984(6)	0.027(5)	0.035(6)	0.037(6)	−0.003(5)	−0.001(4)	0.000(5)
C5a′	0.3470(15)	0.7881(7)	0.4443(8)	0.060(8)	0.046(7)	0.054(8)	−0.028(6)	−0.012(6)	−0.010(6)
C6a	0.0521(15)	0.7900(7)	0.4010(7)	0.056(8)	0.049(7)	0.031(6)	−0.010(5)	−0.002(5)	−0.001(6)
N1b	−0.0991(10)	0.4118(6)	0.4162(6)	0.024(5)	0.063(6)	0.043(6)	0.009(5)	−0.001(4)	−0.007(4)
C1b′	−0.2552(16)	0.3754(9)	0.4235(9)	0.054(9)	0.097(12)	0.069(9)	0.035(9)	−0.005(7)	−0.042(8)
C2b	−0.0809(13)	0.4596(6)	0.3486(7)	0.038(6)	0.044(7)	0.033(6)	0.002(5)	0.007(5)	0.001(5)
O2b′	−0.1928(8)	0.4688(5)	0.2944(5)	0.023(4)	0.078(6)	0.052(5)	0.038(5)	−0.009(4)	−0.013(4)
N3b	0.0632(9)	0.4955(5)	0.3409(5)	0.027(4)	0.030(5)	0.028(4)	0.007(4)	−0.001(4)	−0.001(4)
C4b	0.1908(12)	0.4787(6)	0.3943(6)	0.032(6)	0.030(6)	0.028(5)	−0.000(4)	−0.001(4)	−0.000(4)
O4b′	0.3281(8)	0.5047(4)	0.3842(5)	0.024(4)	0.045(4)	0.045(4)	0.008(4)	0.000(3)	−0.004(3)
C5b	0.1770(13)	0.4279(6)	0.4652(7)	0.037(6)	0.046(7)	0.029(6)	−0.001(5)	0.000(5)	−0.005(5)
C5b′	0.3154(15)	0.4081(8)	0.5253(8)	0.042(7)	0.068(9)	0.051(8)	0.015(7)	−0.027(6)	−0.002(6)
C6b	0.0277(14)	0.3977(6)	0.4735(7)	0.054(7)	0.043(7)	0.038(6)	0.008(5)	−0.006(5)	−0.008(6)
N20	0.2847(15)	0.4986(9)	−0.0131(7)	0.060(8)	0.103(11)	0.048(7)	−0.025(7)	0.014(6)	0.009(7)
O20	0.2931(17)	0.4742(13)	−0.0789(10)	0.083(10)	0.379(26)	0.106(12)	−0.131(16)	0.001(9)	0.022(13)
O21	0.3403(19)	0.4723(9)	0.0549(9)	0.132(12)	0.164(13)	0.074(9)	0.049(9)	−0.015(8)	−0.011(10)
O22	0.2141(33)	0.5493(13)	−0.0040(12)	0.463(40)	0.279(25)	0.141(18)	0.055(16)	0.151(22)	0.266(27)
N30	0.2651(17)	0.7979(7)	0.1823(8)	0.091(10)	0.043(7)	0.063(8)	0.016(6)	0.013(8)	−0.003(7)
O30	0.2973(12)	0.7472(6)	0.1351(7)	0.078(7)	0.052(6)	0.100(8)	−0.019(6)	0.003(6)	0.001(5)
O31	0.3669(23)	0.8323(8)	0.2238(8)	0.255(20)	0.123(12)	0.068(8)	0.008(8)	−0.026(10)	−0.115(14)
O32	0.1275(22)	0.8159(8)	0.1842(10)	0.202(17)	0.119(12)	0.134(13)	0.065(10)	0.085(13)	0.071(12)

*The temperature factor has the form $T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)\}$.

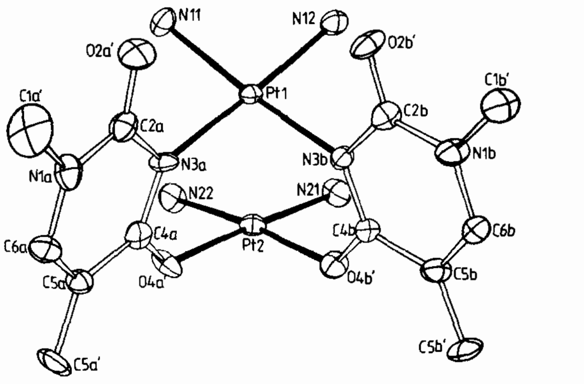

Fig. 2. Molecular cation *cis*-$[(NH_3)_2Pt(1\text{-}MeT)]_2^{2+}$ (head–head).

94.33(2)°, D_c = 2.424 g cm^{-3} for Z = 4 and mol. wt. 860.66, D_m = 2.45 g cm^{-3}. Intensity data were recorded using a $\theta/2\theta$ scan technique ($2\theta \leqslant 50°$, scan width 1°, 2°/min in 2θ, 10 sec background counts at the limits of the scan). There was no significant change in intensity of three check reflections measured every 30 min. 4113 unique reflections were obtained. Lp and an empirical absorption correction (based on ψ scans for 6 reflections with χ settings near 90°, μ = 115.1 cm^{-1}) were applied to I and σ(I) values. 3534 reflections with $F_o \geqslant 2\sigma(F_o)$ were used for the subsequent calculations.

The positions of the Pt atoms were determined from a Patterson map. The remaining non-hydrogen atoms were located by means of F_c calculations and Fourier maps. Hydrogen atoms were not considered at any stage. Least squares refinement gave the parameters listed in Table I. The structure was refined to R = 0.046, R_w(F) = 0.050 (for 3534 reflections with F $\geqslant 2\sigma$(F), 308 parameters, w = $1/(\sigma^2(F) + 0.0007\ F^2)$). The maximum e/Å^3 was 1.7 (0.9 Å away from Pt1). Scattering factors were taken from Cromer and Mann [6], Δf' and Δf" corrections applied [7], and the Shelx-76 program package [8] used.

Since 1-MeT has a pseudo-twofold axis through N3 and C6, the possibility that N1 and C5 atoms might be interchanged, has been considered [5]. This would imply that Pt coordination takes place trhough N3 and O2 and not, as assumed (*vide infra*) through N3 and O4. However, such a possibility seems unlikely for two reasons: first, treatment of N1a and N1b as C atoms leads to unacceptably low temperature factors of these atoms, and second, the R value increases from 0.046 to 0.049.

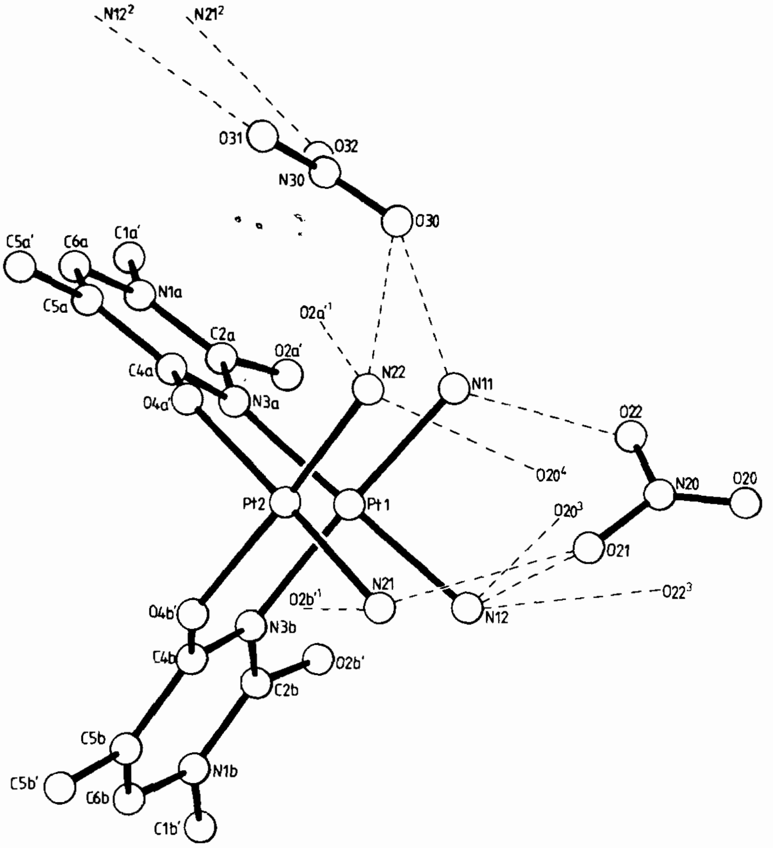

Fig. 3. Projection of the title compound along the Pt1, Pt2 vector. Possible hydrogen bonds between the molecular cation and surrounding nitrate groups are indicated. Symmetry transformations are given in Table IV.

TABLE II. Interatomic Distances (Å) and Angles (deg).

(a) Coordination sphere

Pt1–Pt2	2.927(1)	Pt1–Pt2–O4b′	80.2(2)
Pt1–N11	2.060(9)	N21–Pt2–N22	89.7(4)
Pt1–N12	2.047(9)	N21–Pt2–O4a′	177.3(3)
Pt1–N3a	2.031(8)	N21–Pt2–O4b′	90.4(3)
Pt1–N3b	2.042(8)	N22–Pt2–O4a′	90.6(3)
Pt2–N21	2.031(9)	N22–Pt2–O4b′	174.0(3)
Pt2–N22	2.037(9)	O4a′–Pt2–O4b′	88.9(3)
Pt2–O4a′	2.012(7)		
Pt2–O4b′	2.023(7)		
Pt2–Pt1–N11	102.9(3)		
Pt2–Pt1–N12	100.1(3)		
Pt2–Pt1–N3a	81.5(2)		
Pt2–Pt1–N3b	81.6(2)		
N11–Pt1–N12	89.5(3)		
N11–Pt1–N3a	89.5(3)		
N11–Pt1–N3a	89.5(3)		
N11–Pt1–N3b	175.1(3)		
N12–Pt1–N3a	178.2(3)		
N12–Pt1–N3b	87.8(3)		
N3a–Pt1–N3b	93.1(3)		
Pt1–Pt2–N21	102.5(2)		
Pt1–Pt2–N22	105.6(2)		
Pt1–Pt2–O4a′	80.0(2)		

(b) Ligand geometry

N1a–C1a′	1.489(17)	Pt1–N3a–C4a	126.2(7)
N1a–C2a	1.367(15)	Pt1–N3a–C2a	114.9(6)
C2a–O2a′	1.249(14)	C4a–N3a–C2a	118.9(9)
C2a–N3a	1.409(13)	O4a′–C4a–C5a	119.2(9)
N3a–C4a	1.365(13)	O4a′–C4a–N3a	120.5(9)
C4a–O4a′	1.259(12)	C5a–C4a–N3a	120.2(9)
C4a–C5a	1.438(14)	Pt2–O4a′–C4a	131.6(6)
C5a–C5a′	1.525(16)	C5a′–C5a–C6a	123.5(10)
C5a–C6a	1.343(16)	C5a′–C5a–C4a	118.0(9)
C6a–N1a	1.382(15)	C6a–C5a–C4a	118.4(9)
		N1a–C6a–C5a	121.7(10)
N1b–C1b′	1.475(17)		
N1b–C2b	1.380(15)	C1b′–N1b–C2b	118.6(9)
C2b–O2b′	1.238(13)	C1b′–N1b–C6b	121.5(10)
C2b–N3b	1.383(14)	C2b–N1b–C6b	119.9(9)
N3b–C4b	1.350(12)	O2b′–C2b–N3b	120.4(10)
C4b–O4b′	1.265(12)	O2b′–C2b–N1b	119.8(10)
C4b–C5b	1.449(15)	N3b–C2b–N1b	119.8(9)
C5b–C5b′	1.491(16)	Pt1–N3b–C4b	125.4(7)
C5b–C6b	1.381(16)	Pt1–N3b–C2b	113.7(6)
C6b–N1b	1.372(16)	C4b–N3b–C2b	120.5(8)
		O4b′–C4b–N3b	122.2(9)
C1a′–N1a–C2a	116.4(10)	O4b′–C4b–C5b	116.7(9)
C1a′–N1a–C6a	123.3(10)	C5b–C4b–N3b	121.0(9)
C2a–N1a–C6a	120.2(9)	Pt2–O4b′–C4b	129.9(6)
O2a′–C2a–N3a	120.2(10)	C5b′–C5b–C6b	121.5(10)
O2a′–C2a–N1a	120.0(10)	C5b′–C5b–C4b	122.5(10)
N3a–C2a–N1a	119.8(9)	C6b–C5b–C4b	116.1(9)
		C5b–C6b–N1b	122.4(10)

(continued on facing page)

TABLE II. *(continued)*

(c) Anion geometry

N20–O20	1.136(21)	O20–N20–O21	128.1(18)
N20–O21	1.233(18)	O20–N20–O22	120.3(18)
N20–O22	1.088(22)	O21–N20–O22	111.6(16)
N30–O30	1.209(17)	O30–N30–O31	121.7(15)
N30–O31	1.204(21)	O30–N30–O32	118.1(14)
N30–O32	1.204(23)	O31–N30–O32	120.1(15)

TABLE III. Conformational Parameters.*

(a) Deviations of Pt atoms from least squares coordination planes.

ΔPt1 0.050 Å from N11, N12, N3a, N3b (plane I)[a]
ΔPt2 −0.077 Å from N21, N22, O4a', O4b' (plane II)[b]

(b) Deviations of Pt atoms from least squares 1-MeT planes

ΔPt1 −0.172 Å, ΔPt2 −0.061 Å from N1a, C2a, N3a, C4a, C5a, C6a (plane III)[c]
ΔPt1 −0.032 Å, ΔPt2 −0.402 Å from N1b, C2b, N3b, C4b, C5b, C6b (plane IV)[d]

(c) Dihedral angles

plane I/plane III	77.26°
plane I/plane IV	72.42
plane II/plane III	80.29
plane II/plane IV	84.33
plane I/plane II	31.37
plane III/plane IV	94.37

(d) Torsional angles

N11, Pt1, Pt2, N22	−1.2°
N12, Pt1, Pt2, N21	−2.6

*Equations of the planes refer to the *a b c* basis. [a]$8.4178x - 0.5103y - 0.8000z = 0.030$. [b]$7.0992x + 1.0159y + 7.4573z = 5.677$. [c]$2.1615x + 10.0391y - 12.6541z = 2.977$. [d]$-2.4768x + 13.5634y + 9.2739z = 9.706$.

Results and Discussion

Molecular Structure

In Fig. 2 a view of the dinuclear cation perpendicular to the Pt1–Pt2 axis is given, in Fig. 3 the cation is viewed along the Pt2–Pt1 vector. Table I lists atomic parameters, Table II selected interatomic distances and angles, and Table III conformational parameters. The cation consists of two *cis*-$(NH_3)_2$-Pt(II) units each bridged by two 1-methylthyminato ligands through N3 and O4, with the 1-MeT ligands arranged in head-head fashion. The intramolecular Pt–Pt distance is 2.927(1) Å and both Pt atoms are slightly out (av. 0.06 Å) of their coordination planes, directed towards each other. The Pt coordination planes are substantially tilted (31.4°), but nearly eclipsed (twist angle about the Pt–Pt vector av. 1.9°). This feature, which can be seen particularly well in Fig. 3, is unique for the 1-MeT dimer and is not observed in any of the other structures of related compounds. In these compounds, the Pt coordination planes are twisted by angles between 20 and 25°. The 1-MeT rings are essentially planar. Pt1, which binds to the 1-MeT rings through N3, is almost coplanar with one of the two rings (b), but significantly out of the plane of the other (ring a), 0.032 Å vs. 0.172 Å. With Pt2, bound through O4, conditions are reversed; while it is only slightly out of the plane of ring a, it is markedly displaced out of the plane of ring b, 0.061 Å *vs.* 0.402 Å. The two 1-MeT planes are almost perpendicular to each other, while the dihedral angles between the Pt coordination planes and the 1-MeT planes range from 72° to 84°.

Within the two 1-MeT rings, bond lengths and angles do not differ significantly. Compared with neutral 1-methylthymine [9], no great changes in bond lengths occur on Pt binding, but the trend in

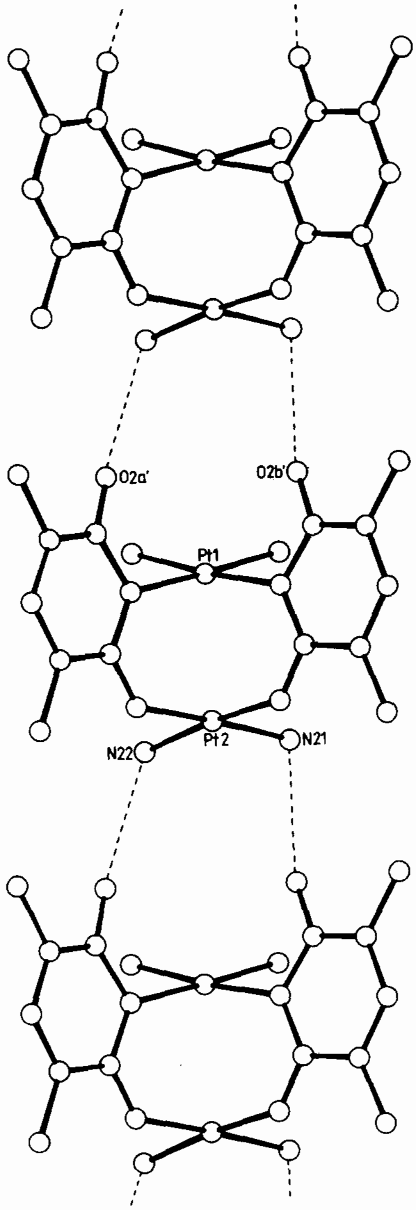

Fig. 4. Arrangement of molecular cations of *cis*-$[(NH_3)_2Pt(1\text{-}MeT)]_2^{2+}$. Hydrogen bonding occurs between the exocyclic O2 sites of one cation with the NH_3 groups N21 and N22 of the adjacent cation.

TABLE IV. Possible Hydrogen Bonding Interactions.*

(a) Between NH_3 and O2			
N22–O2a'^{1}	2.85 Å	Pt2–N22···O2a'^{1}	110.5°
N21–O2b'^{1}	2.83	Pt2–N21···O2b'^{1}	99.8
(b) Between NH_3 and NO_3^-			
N11–O30	2.97 Å	Pt1–N11···O30	110.7°
N11–O22	2.91	Pt1–N11···O22	110.1
N12–O21	3.11	Pt1–N12···O21	104.9
N21–O21	3.01	Pt2–N21···O21	103.6
N22–O30	2.93	Pt2–N22···O30	109.8
O31–N12^2	2.99	N30–O31···N12^2	147.4
O32–N21^2	3.11	N30–O32···N21^2	123.5
N12–O20^3	3.28	Pt1–N12···O20^3	88.8
N12–O22^3	3.27	Pt1–N12···O22^3	120.7
N22–O20^4	3.10	Pt2–N22···O20^4	113.8

*Symmetry transformations: ^{1}1 + x, y, z; ^{2}0.5 – x, 0.5 + y, 0.5 – z; ^{3}–x, 1 – y, –z; ^{4}1 – x, 1 – y, –z.

changes of angles in the vicinity of the Pt coordination sites is the same as in the corresponding head–tail dimers of 1-MeT [10] and 1-MeU [14]. Specifically, the internal 1-MeT angles at C2, N3, and C4 are all close to 120° (*e.g.* N1, C2, N3: 119.8° (ring a and ring b); C2, N3, C4: 118.9° (a), 120.5° (b); N3, C4, C5: 120.2° (a), 121.0° (b)), whereas in the neutral 1-methylthymine these angles exhibit an alternating pattern (115.4°, 126.3°, 116.1°). Dimers of the title compound are arranged as shown in Fig. 4, forming infinite strands. Within a strand, dimers are held together by moderately strong hydrogen bonds (2.83 and 2.85 Å) between the non-coordinating exocyclic O2 oxygens of the 1-MeT rings and NH_3 groups of the neighboring cation. Different dimer strands are linked through a network of hydrogen bonds formed between the NH_3 groups and the nitrate oxygens (Table IV).

There are two structural aspects of this head–head dimer that deserve some further comment. The very small torsional angle between the Pt coordination planes, leading to a nearly eclipsed conformation, and the hydrogen bonding pattern between adjacent dimers.

Hollis and Lippard, in a series of papers of various α-pyridone complexes of *cis*-$(NH_3)_2Pt$, have shown that in their system a relationship exists between the Pt–Pt distance within the dimer and the geometric parameters tilt angle τ and torsional angle (or twist angle) ω of the Pt coordination planes. With decreasing Pt–Pt separation the tilt angle between adjacent Pt planes decreases whereas the torsional angle about the Pt–Pt vector simultaneously increases [2, 11, 12]. Although this relationship is not linear, it holds up both for head–head and head–tail α-pyridone dimers, unless a high interplanar steric repulsion is involved as, for example, on substitution of the two ammines by ethylenediamine [13]. Then the Pt–Pt distance, the tilt and the torsional angle increase simultaneously compared to the diammine analogue. A comparison of related 1-methyluracil (1-MeU) dimers, the head–tail dimer *cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_2(NO_3)_2$ [14], a heteronuclear derivative, *cis*-$[(NH_3)_2Pt(1\text{-}MeU)Ag]_2(NO_3)_4$ [15], which contains Ag bound to both O2 sites of the 1-MeU rings, and a diplatinum(III) oxidation product, *cis*-$[(H_2O)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(NO_2)](NO_3)_3$ [16] indicates agreement with the

TABLE V. Comparison of Geometric Parameters of Various 1-MeT and 1-MeU Complexes of *cis*-$(NH_3)_2Pt$.[a]

	$Pt{-}Pt_{intra}$	τ[b]	ω[c]	Ref.
$[(NH_3)_2Pt(1\text{-}MeT)]_2(NO_3)_2$ (head–head)	2.927(1)	31.4	1.9	d
$[(NH_3)_2Pt(1\text{-}MeU)]_2(NO_3)_2$ (head–head)	2.937(1)	34.1	25.2	4
$\{Ag[Pt(NH_3)_2(1\text{-}MeU)]_4\}(NO_3)_5$ (head–head)	2.949(2)	31.5	4.5	17
$[(NH_3)_2Pt(1\text{-}MeT)]_2(NO_3)_2$ (head–tail)	2.974(1)	36.1	13.8	10
	2.920(1)[e]	35.2	25.7	18
	2.915(1)[e]	30.7	17.9	18
$[(NH_3)_2Pt(1\text{-}MeU)]_2(NO_3)_2$ (head–tail)	2.954(2)	35.8	20.5	14
$[(NH_3)_2Pt(1\text{-}MeU)Ag]_2(NO_3)_4$ (head–tail)	2.892(1)	29.8	24.3	15
$[(H_2O)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(NO_2)](NO_3)_3$ (head–tail)	2.574(1)	21.5	31.5	16

[a] Distances in Å, angles in deg. [b] Tilt angle between Pt coordination planes. [c] Average torsional angle about Pt–Pt vector. [d] This work. [e] Two crystallographically independent dimers.

trends observed with the *cis*-$(NH_3)_2Pt$ complexes of α-pyridone. On the other hand, the two presently available structures containing head–head arranged 1-MeU ligands in complexes of *cis*-$(NH_3)_2Pt(II)$ do not follow this trend, and data of two structures of head–tail 1-MeT dimers with three crystallographically different dimer units are contradictory (Table V). For example, the Pt–Pt distance in the head–head dimer *cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_2(NO_3)_2$ (2.937 Å) [4] slightly increases in *cis*-$\{Ag[Pt(NH_3)_2(1\text{-}MeU)]_4\}(NO_3)_5 \cdot 4H_2O$, which contains two dimers linked through the available O2 sites by Ag, to 2.949 Å [17], yet the tilting of the Pt coordination planes (by 2.6°) and, most dramatically, the torsion angle (by 20.7°) decrease simultaneously. With the head–tail dimers *cis*-$[(NH_3)_2Pt(1\text{-}MeT)]_2(NO_3)_2$ [10, 18] Pt–Pt distances of 2.974, 2.920 and 2.915 Å and tilt angles of 36.1, 35.2 and 30.7°, respectively, agree with the sequence observed with the α-pyridone complexes of *cis*-$(NH_3)_2Pt$ and the head–tail 1-MeU compounds, yet the torsional angles do not: they are 13.8, 25.7 and 17.9°. Since particular steric interactions between the Pt coordination planes in 1-MeU and 1-MeT complexes cannot account for these discrepancies – all complexes contain the identical *cis*-$(NH_3)_2Pt$ moiety – manipulations at the O2 oxygens seem to be the most plausible reason for the observed combinations of Pt–Pt distance, τ, and ω. Indeed, Ag linking the two O2 atoms of the two 1-MeU planes in the head–head dimer forces these ligands into a more rigid structure than does Pt binding to N3 and O4 alone, leading to a very small torsion angle of 4.5° in the Pt_4, Ag compound. Hydrogen bonding at the available O2 sites should have a similar effect. Thus differences in hydrogen bonding patterns of the O2 oxygens in the three 1-MeT head–tail structures might account for the observed values of the torsional angles. Finally, the flexibility of the Pt1–N3–C4–O4–Pt2 moiety, which manifests itself in the different degrees of Pt deviations from the ligand planarity (*cf.* Table III), probably is another factor influencing the Pt–Pt separation, the tilt of the Pt coordination planes, and their torsion.

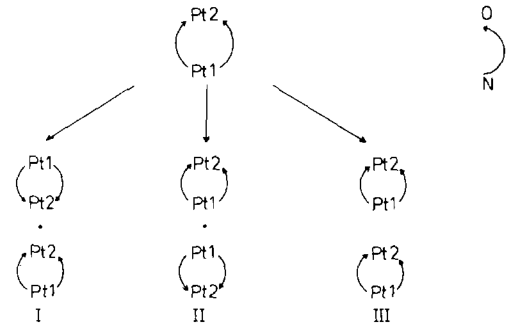

Fig. 5. Three possible arrangements of head–head dimers: (I) Centrosymmetric arrangement with O-coordinating sites next to each other. (II) Centrosymmetric arrangement with N-coordinating sites next to each other. (III) Arrangement with N- and O-coordinating sites next to each other.

As for the packing of the 1-MeT head–head dimer, it is quite different from that in related head–head dimers. The published structures can be divided into three groups, differing in their respective hydrogen bonding patterns, which are interrelated according to the scheme presented in Fig. 5. The principal features of these three types are:

– Type I. Centrosymmetric arrangement of two head-head dimers with the O-coordinating Pt2 atoms next to each other, leading to a (Pt1, Pt2)·(Pt2, Pt1) sequence.

– Type II. Centrosymmetric arrangement of two dimers with the N-coordinating Pt1 atoms next to each other, leading to a (Pt2, Pt1)·(Pt1, Pt2) sequence.

– Type III. Dimers arranged in (Pt2, Pt1), (Pt2, Pt1), ... sequence.

Examples of type I are the head-head dimers of α-pyridone with Pt in its oxidation states +2 [2a] and +2.25 [2b], respectively, of 1-methylhydantoin (Pt oxidation state +2) [19], and of α-pyrrolidone (Pt oxidation state +2.5) [3]. In these compounds, two dimers are held together by hydrogen bonds between NH_3 groups and the Pt-coordinating oxygens of the neighbor and by metal–metal bonding, respectively. Intermolecular Pt–Pt distances are short, ranging from 3.20 [19] in $Pt^{2.0}$ complexes to 2.71 Å [3] in the $Pt^{2.5}$ compound.

Type II is realized in the 1-MeU head–head dimer [4]. There, hydrogen bonding between 4 NH_3 groups and 4 non-coordinating oxygens of adjacent units holds two dimers together. Because of the steric demand of these oxygens and their mutual repulsion, the intermolecular Pt–Pt distance is considerably larger, *e.g.* 4.8 Å in the 1-MeU dimer.

The 1-MeT dimer discussed here represents an example of Type III. Hydrogen bonds are formed between 2 NH_3 groups of one dimer and 2 noncoordinating oxygens of the adjacent dimer. The intermolecular Pt–Pt separation is large, *e.g.* 5.66 Å in our compound.

While the hydrogen bonding pattern of the head–head dimers containing ligand with a single amidate group (α-pyridone and α-pyrrolidone) is not unexpected, it is surprising that the 1-MeU and 1-MeT head–head dimers seem to avoid this pattern. Rather, the still available second exocyclic oxygen is used as proton acceptor, in a manner very similar to that for the head–tail 1-MeU and 1-MeT dimers. Only if the O2 site is not available for hydrogen bonding is there a type I pattern, for example between pentanuclear Pt_4, Ag units in cis-$\{Ag[Pt(NH_3)_2(1\text{-MeU})]_4\}(NO_3)_5$ [17] (intermolecular Pt–Pt separation 3.25 Å). 1-Methylhydantoin, which has a great structural similarity to 1-MeT, on the other hand, prefers type I over II or III, which are in principle feasible as well. It should be interesting to find out if 1-MeU and 1-MeT ligands always behave in the above described way or if factors such as solvent, degree of hydration, counter ion(s) *etc.* affect the crystallization pattern as well. Such studies are currently underway.

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