Formation and X-ray crystal structure analysis of a Pt(IV) complex of 1-methylthymine, obtained through Au(III) treatment of a Pt(II) complex

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Abstract

The crystal structure of *cis,cis*-$[(NH_3)_2Pt(1\text{-MeT})_2(OH)(H_2O)]AuCl_4 \cdot H_2O$, where 1-MeT is the anion of 1-methylthymine, $C_6H_7N_2O_2$, is reported. The compound contains both heterocyclic bases bound to Pt via the N3 positions, the two nucleobase ligands being in a head-to-head orientation. It represents the first X-ray structurally characterized example of a Pt(IV) species of thymine. The compound crystallizes in the space group $P\bar{1}$ with unit cell dimensions $a=8.435(4)$, $b=11.884(3)$, $c=12.869(7)$ Å, $\alpha=97.28(3)$, $\beta=91.66(5)$, $\gamma=110.66(5)°$, $V=1193(2)$ Å^3.

Introduction

Polynuclear complexes of *cis*-$(NH_3)_2Pt(II)$ with the pyrimidine nucleobases uracil and thymine have been systematically studied for several reasons, e.g. the elucidation of 'platinum pyrimidine blues', the question of Pt oxidation state and its stabilization in these compounds and the interaction of Pt and heterometals in related heteronuclear systems [1]. We have shown that *cis*-$(NH_3)_2Pt(II)L_2$, where L are the deprotonated forms of the model nucleobases 1-methylthymine (1-MeT) or 1-methyluracil (1-MeU), can be used as building blocks for the synthesis of dinuclear Pt(II) complexes by condensation reactions with several mononuclear Pt complexes [2]. These dinuclear Pt(II) complexes show a challenging oxidation behaviour, as they form a variety of larger aggregates through partial oxidation and formation of intermolecular Pt–Pt bonds [3]. There has also been a growing interest in heteronuclear complexes of gold and other transition metals like Pt, complexes which may have bridging ligands between gold and a second metal and may contain metal–metal bonds, mainly because of their possible role in catalysis.

Our attempts to prepare a heteronuclear Pt,Au complex focused on the possibility of a Pt(III),Au(III) complex being formed, which would be an analogue of a dinuclear Pt(II),Pt(III) complex. Au(III) is isoelectronic with Pt(II), however, in contrast to Pt(II) it cannot be oxidized further. Thus according to

$$\text{Pt(II),Au(III)} \xrightarrow{-e^-} \text{Pt(III),Au(III)}$$

the preparation of a dinuclear Pt(III),Au(III) complex, representing the analogue of a never isolated dinuclear $[Pt(2.5)]_2$ complex with one unpaired electron, might be feasible. Previous results show that mixed-valence Pt complexes are stabilized with formation of a tetranuclear structure [4].

We have shown that *cis*-$(NH_3)_2Pt(1\text{-MeT})_2$ reacts with $PtCl_4^{2-}$, resulting in the formation of the dinuclear Pt(II) complex *cis*-$(NH_3)_2Pt(1\text{-MeT})_2PtCl_2$ [2]. We therefore studied the reaction behaviour of the isoelectronic Au(III) entity towards the *cis*-$(NH_3)_2Pt(1\text{-MeT})_2$ unit.

We were aware that various possibilities exist. (i) Formation of the dinuclear species *cis*-$[(NH_3)_2Pt(1\text{-MeT})_2AuCl_2]Cl$. (Because of the tendency of Au(III) to form five- or six-coordinated species [5], larger aggregates seemed possible as well.) (ii) Occurrence of oxidation reactions. As Au(III) is a strong oxidant, platinum(II) complexes can be oxidized to Pt(IV) by $AuCl_4^-$. However, a chloride-assisted process does not always occur [6]. Oxidation of the ligand $-NH_3$ or, less likely, 1-methylthymine– is possible too. (iii) Ligand protonation. This could be followed by loss of a nu-

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cleobase ligand, eventually giving 1:1 complexes or derivatives thereof, very much as in the case of Pt(II) [7].

Reaction of $NaAuCl_4$ with *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2$ yielded, among others, orange crystals, suitable for X-ray analysis. As the characterization by spectroscopic techniques proved to be difficult, we undertook an X-ray analysis.

Experimental

Synthesis

cis-$(NH_3)_2Pt(1\text{-}MeT)_2$ was prepared according to ref. 8a. The title compound was prepared by reacting 0.2 mmol of *cis*-$(NH_3)_2Pt(1\text{-}MeT)_2 \cdot H_2O$ in 15 ml H_2O with 0.2 mmol of $NaAuCl_4$. After filtration from yellowish *cis*-$[(NH_3)_2Pt(1\text{-}MeT)(1\text{-}MeTH)]\,AuCl_4 \cdot H_2O$ (**1**), characterized by elemental analysis (*Anal.* Calc. for $C_{12}H_{23}N_6O_5PtAuCl_4$: C, 16.55; H, 2.40; N, 9.70. Found: C, 16.66; H, 2.68; N, 9.71%) and IR spectroscopy by comparison with *cis*-$[(NH_3)_2Pt(1\text{-}MeT)(1\text{-}MeTH)]X$, X/2 = $PtCl_4^{2-}$, $PtCl_6^{2-}$, the solution (pH 3) was allowed to crystallize at 4 °C. After 3 days, yellow–orange crystals of **2**, suitable for X-ray analysis, were isolated in 23% yield. *Anal.* Calc. for **2**, $C_{12}H_{25}N_6O_7PtAuCl_4$: C, 16.0; H, 2.8; N, 9.4; Cl, 16.7. Found: C, 16.0; H, 2.8; N, 9.4; Cl, 15.8%. IR (cm^{-1}, prominent bands only): 1660, 1590, 1540, 1470, 1440 (double-bond stretching region); 360 (νAuCl). ^1H NMR (D_2O, pD 3.4, ppm): 7.41 (H(6)); 3.32 (N-CH_3); 1.79 (C-CH_3).

Physical measurements

IR spectra were recorded on a Perkin-Elmer spectrometer, ^1H NMR spectra on a Bruker AM 300. The X-ray photoelectron spectroscopic measurements were made with a VG scientific instruments ESCA spectrometer using Al Kα radiation (1486.6 eV) as the X-ray source. The powdered sample was dusted onto double-sided tape. All spectra were taken under a vacuum of about 10^{-8} torr. Binding energies were calibrated to the symmetric C1s line (285.0 eV). No X-ray damage was observed.

Crystallography

A small, poorly diffracting, prismatic crystal was mounted on a glass fibre at a random orientation on an Enraf-Nonius CAD4 diffractometer for the unit cell and space group determinations and for the data collection. Unit cell dimensions were obtained by a least-squares fit of the 2θ values of 25 high order reflections ($8.3 < \theta < 15.1$) using the CAD4 centring routines. Selected crystallographic and other experimental parameters are listed in Table 1.

Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities; the stability of the crystal was measured by monitoring 3 standards every hour. Data have been corrected for Lorentz and polarization factors and for the observed decay. An empirical absorption correction was applied using azimuthal (ψ) scans of two reflections ($\chi > 85.9$). The standard deviations on intensities were calculated in term of statistics alone.

The structure was solved by a combination of Patterson and Fourier methods and refined by full matrix least-squares [9] (the function minimized was $[\Sigma w(|F_o| - 1/k|F_c|)^2]$). No extinction correction was deemed necessary. After refining to convergence the complete structural model with isotropic temperature factors for all atoms, a further empirical Fourier series based absorption correction was applied to the data set using the program DIFABS [9, 10]. For the final cycles of refinement anisotropic temperature factors were used for the Pt and oxygen atoms, the anion and the substituents of the 1-MeT rings, all other atoms being treated isotropically.

The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature [11].

The contribution from the hydrogen atoms in their idealized positions (C–H = 0.95 Å, $B = 1.3 \times B_{eq}$(C bonded) $Å^2$) was taken into account but not refined. Upon convergence (no parameter shift $> 0.2\sigma(p)$) a Fourier difference map showed no significant feature.

All calculations were carried out by using the MOLEN crystallographic package [9].

Final atomic coordinates and thermal factors are given in Table 2. See also 'Supplementary material'.

Results

Reaction of *cis*-$(NH_3)_2PtL_2$ with $NaAuCl_4$ in aqueous solution always led to the formation of a yellowish precipitate, which was identified by IR spectroscopy and elemental analysis as *cis*-$[(NH_3)_2PtL(LH)]AuCl_4$ (**1**). Protonation of the nucleobase ligand through the strongly acidic $AuCl_4^-$ (solvolysis!) cannot be avoided, as pH adjustment leads to the formation of $Au(OH)_x$ precipitates. Buffers proved to be unsuitable, too. In the case of L = 1-MeT, however, it was possible to isolate crystals from the reaction mixture after filtration of **1**. The IR spectrum of this compound **2** was considerably different from **1**; UV spectra showed the π–π* absorption of the nucleobase at 267 nm. Absorptions of Pt(LH) species are typically around 285 nm. $[Pt(III)]_2$ complexes display similar absorptions. For example, for a diplatinum(III) complex containing two L = 1-MeT bridging ligands (N3, O4), an absorption at 267 nm is observed [12].

TABLE 1. Experimental data for the X-ray diffraction study of *cis,cis*-$[(NH_3)_2Pt(1\text{-MeT})_2(OH)(H_2O)][AuCl_4]\cdot H_2O$ (**2**)

Formula	$C_{12}H_{25}AuCl_4N_6O_7Pt$
Molecular weight	899.224
Crystal dimensions (mm)	$0.15 \times 0.10 \times 0.06$
Data collection T (°C)	25
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.435(4)
b (Å)	11.884(3)
c (Å)	12.869(7)
α (°)	97.28(3)
β (°)	91.66(5)
γ (°)	110.66(4)
V (Å^3)	1193(2)
Z	2
ρ(calc.) (g cm^{-3})	2.501
μ (cm^{-1})	127.69
Radiation	Mo Kα (graphite monochromated $\lambda = 0.71069$ Å)
Measured reflections	$+-h,\ +-k,\ +l$
θ Range (°)	$2.5 < \theta < 22.0$
Scan type	$\omega/2\theta$
Scan width (°)	$1.0 + 0.35 \tan \theta$
Max. counting time (s)	70
Background time (s)	0.5* scan-time
Max. scan speed (° min^{-1})	5
Prescan rejection limit	0.50 (2.0σ)
Prescan acceptance limit	0.025 (40.0σ)
Horizontal receiving slit (mm)	$1.80 + \tan \theta$
Vertical receiving slit (mm)	4.0
No. independent data collected	2909
No. obs. reflections (n_o) ($\lvert F_o \rvert^2 > 2.0\sigma(\lvert F \rvert)^2$)	1570
Transmission coefficient	1.252–0.721
Decay corrections	1.358–1.001
No. parameters refined (n_v)	218
R[a]	0.056
R_w[b]	0.065
GOF[c]	1.222

[a] $R = \Sigma(\lVert F_o\rvert - (1/k)\lvert F_c\rVert)/\Sigma\lvert F_o\rvert$. [b] $R_w = [\Sigma w(\lvert F_o\rvert - (1/k)\lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$; $w = [\sigma^2(F_o)]^{-1}$; $\sigma(F_o) = [\sigma^2(F_o^2) + f^4(F_o^2)]^{1/2}/2F_o$ with $f = 0.075$. [c] $GOF = [\Sigma w(\lvert F_o\rvert - (1/k)\lvert F_c\rvert)^2/(n_o - n_v)]^{1/2}$.

ESCA has shown to be a useful tool for the determination of Pt oxidation states from Pt 4f binding energies. ESCA spectra of **2** show the doublet of Pt and Au in a 1:1 ratio, the splitting of the Pt doublets is 3.2 eV, of the Au doublets 3.6 eV, consistent with the literature [13]. Pt(II) complexes have Pt($4f_{7/2}$) binding energies between 72.4 and 74.3 eV [14], Pt(IV) complexes between 75.5 and 76.7 eV.

For **2**, a Pt binding energy of 73.8 eV was measured, a value more in the Pt(II) range. The Au ($4f_{7/2}$) value was measured to be 85.1 eV, thus being a little lower than the value typically expected for an Au(III) chloro complex (87.3 eV for $KAuCl_4$, 84.3–87.8 for several Au(III) complexes, and 84.2–85.1 for Au(I) complexes [15, 16]). From these data a possible interaction between Pt and Au could not be ruled out. Specifically, the oxidation state of the two metals remained unclear. The X-ray analysis of **2** finally showed that there was no interaction between the two metal centres. Rather, the starting material was oxidized by Au(III) to the platinum(IV) compound **2**. Figure 1 shows the molecular cation of **2** and the atom numbering scheme. Selected bond lengths and angles are given in Table 3. Coordination of Pt is through the deprotonated N3 position of the two 1-methylthyminato ligands, which are in *cis* position to each other. Two nitrogens of the ammine ligands and the two axial oxygens complete the almost octahedral coordination sphere of Pt(IV). Pt–NH_3 and Pt–N(nucleobase) distances are normal and compare well with data on related compounds [17–20]. Dihedral angles between the nucleobases and the PtN_4 coordination plane are 55° (ring with N3) and 52° (ring with N3a), expectedly smaller than in Pt(II) complexes and a consequence of steric interference of exocyclic nucleobase oxygens and axial O(1) and O(3) oxygens [19b].

TABLE 2. Final positional parameters and equivalent isotropic temperature factors for **2** with e.s.d.s given in parentheses

Atom	*x*	*y*	*z*	*B* (Å^2)
Au1	1.000	0.500	0.500	4.12(5)
Au2	1.500	0.500	1.000	5.10(5)
Pt1	0.7763(1)	−0.0193(1)	0.36329(9)	2.34(2)
Cl11	1.211(1)	0.4350(8)	0.4516(9)	7.0(3)
Cl12	1.081(1)	0.6471(8)	0.3968(8)	6.6(3)
Cl21	1.332(1)	0.602(1)	1.061(1)	9.3(4)
Cl22	1.686(2)	0.5905(9)	1.142(1)	9.3(4)
O1	0.518(2)	−0.111(2)	0.332(2)	4.0(5)
O2a	1.007(2)	0.174(1)	0.232(1)	3.4(5)
O2	1.030(2)	−0.135(2)	0.264(2)	5.0(5)
O3	1.018(2)	0.068(2)	0.399(1)	3.8(5)
O4	0.564(2)	−0.065(2)	0.152(2)	4.5(5)
O4a	0.540(2)	0.128(2)	0.414(2)	5.2(6)
O5	0.455(4)	−0.345(2)	0.332(2)	8.5(8)*
N1	0.981(3)	−0.141(2)	0.088(2)	4.7(6)*
N1a	0.886(3)	0.313(2)	0.232(2)	3.9(5)*
N2	0.760(3)	0.042(2)	0.517(2)	3.6(6)
N3a	0.772(2)	0.139(2)	0.316(2)	2.4(4)*
N3	0.801(3)	−0.089(2)	0.204(2)	3.6(5)*
N4	0.797(3)	−0.174(2)	0.413(2)	4.5(7)
C1	1.126(4)	−0.182(3)	0.075(3)	7(1)
C1a	1.026(4)	0.394(3)	0.180(3)	4.9(9)
C2	0.947(4)	−0.121(2)	0.193(2)	3.6(6)*
C2a	0.888(3)	0.205(2)	0.258(2)	3.0(6)*
C4a	0.643(4)	0.175(3)	0.350(3)	4.0(7)*
C4	0.697(3)	−0.084(2)	0.133(2)	2.7(6)*
C5	0.723(3)	−0.123(2)	0.028(2)	2.6(6)*
C5a	0.629(3)	0.281(2)	0.315(2)	3.3(6)*
C5′	0.603(5)	−0.132(3)	−0.064(3)	6.2(9)
C5a′	0.482(4)	0.319(3)	0.346(4)	7(1)
C6	0.863(4)	−0.146(3)	0.005(3)	4.3(7)*
C6a	0.756(4)	0.346(3)	0.260(2)	3.9(7)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1)+b^2\beta(2,2)+c^2\beta(3,3)+ab(\cos\gamma)\beta(1,2)+ac(\cos\beta)\beta(1,3)+bc(\cos\alpha)\beta(2,3)]$.

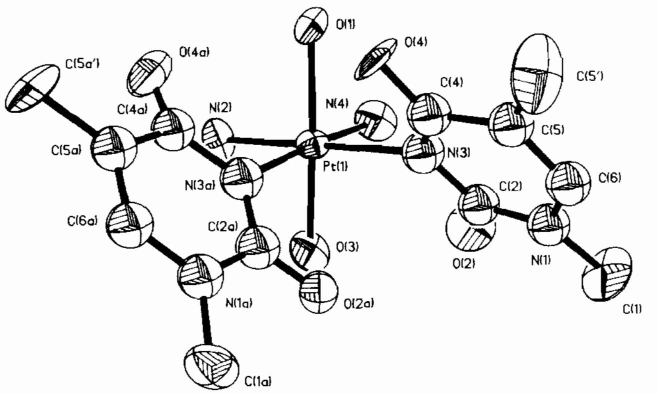


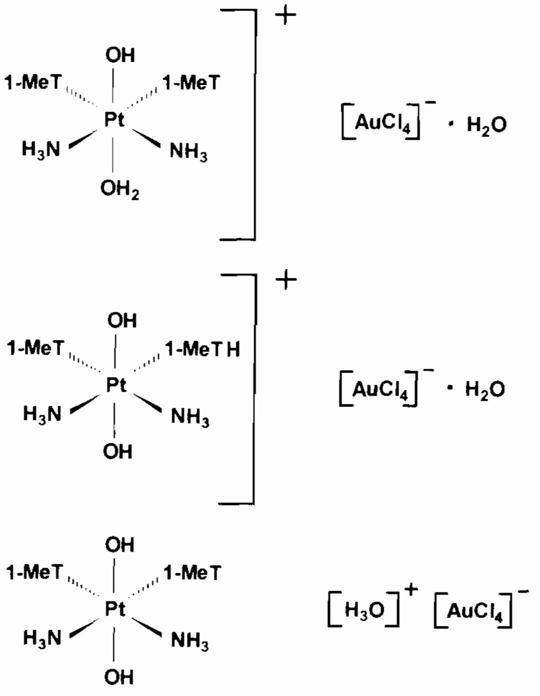
Fig. 1. View of the *cis,cis*-$[(NH_3)_2Pt(1\text{-}MeT)_2(OH)(H_2O]^+$ cation with atom numbering scheme.

Since it proved impossible to locate the hydrogen atoms of the axial ligands, the coordination sphere of Pt is not unambiguous. Three possibilities must be

TABLE 3. Interatomic distances (Å) and angles (°) in **2**

Pt coordination sphere			
Pt–O1	2.07(2)	O1–Pt–N2	94.8(8)
Pt–O3	1.94(2)	O1–Pt–N3	86.5(8)
Pt–N2	2.05(2)	O1–Pt–N4	89.2(9)
Pt–N4	2.08(3)	O1–Pt–N3a	94.3(8)
Pt–N3	2.15(2)	O3–Pt–N2	82.8(8)
Pt–N3a	2.06(2)	O3–Pt–N3	95.9(8)
		O3–Pt–N3a	86.1(8)
O1–Pt–O3	177.6(8)	O3–Pt–N4	90.4(9)
N2–Pt–N3	177.1(1.1)	N2–Pt–N3a	91.8(9)
N3a–Pt–N4	176.5(8)	N2–Pt–N4	87.9(1.0)
		N3–Pt–N3a	90.6(9)
		N3–Pt–N4	89.6(1.0)
Thymine ligands			
N3–C2	1.41(4)	N3a–C2a	1.34(3)
N3–C4	1.27(4)	N3a–C4a	1.36(4)
N1–C2	1.40(4)	N1a–C2a	1.38(4)
N1–C6	1.41(4)	N1a–C6a	1.33(4)
C4–C5	1.43(4)	C4a–C5a	1.44(5)
C5–C6	1.34(5)	C5a–C6a	1.35(4)
N1–C1	1.48(5)	N1a–C1a	1.47(4)
C2–O2	1.19(4)	C2a–O2a	1.23(4)
C4–O4	1.25(3)	C4a–O4a	1.25(4)
C5–C5′	1.50(4)	C5a–O5a′	1.50(5)
$AuCl_4^-$ anion			
Au1–Cl11	2.249(9)	Cl11–Au1–Cl12	91.5(4)
Au1–Cl12	2.255(10)	Cl11–Au1–Cl12*	88.5(4)
Au2–Cl21	2.255(10)	Cl21–Au2–Cl22	89.7(5)
Au2–Cl22	2.264(12)	Cl21–Au2–Cl22*	90.3(6)

Atoms Cl12* and Cl22* are obtained by the symmetry operations: $1-x$, $-y$, $-z$ and $1-x$, $1-y$, $1-z$, respectively.



(1)

(2)

(3)

Fig. 2. Feasible compositions of the title compound.

considered (Fig. 2). Possibility (3) is considered least likely as there are no short hydrogen bonding contacts involving O(5) (cf. Table 4), in particular no such one in which O(5) acts as an H donor. Rather, in the H bond of 2.94 Å between $NH_3(4)$ and O(5), O(5) acts as an acceptor. It is more difficult to rule out possibility (2). Although, in principle, it should be possible to differentiate between the anionic 1-MeT and the neutral 1-MeTH ligand on the basis of their geometries (cf. situation in *cis*-$[(NH_3)_2Pt(1\text{-MeT})(1\text{-MeTH})]^+$ [8] or *cis*-$[(NH_3)_2Pt(1\text{-MeU})(1\text{-MeUH})]^+$ [7], with 1-MeUH = 1-methyluracil), the acidic proton of 1-MeTH could be disordered over both rings, even though this is not realized in three previously solved structures. As with (3), there is no convincing argument from H bonding considerations, that (2) is the correct description of the situation in the solid state. This leaves (1) as the most reasonable possibility: the Pt–O(1) (2.06(2) Å) and Pt–O(3) (1.94(2) Å) separations are sufficiently different (4.3 σ) to tentatively assign O(3) to a hydroxo ligand and O(1) to an aqua group. Comparison with related *trans*-$Pt^{IV}(OH)_2$ compounds [17, 18, 20, 21] seems to justify this interpretation. However, we are aware, that a disorder of OH and H_2O is feasible, in principle. The packing diagram (Fig. 3) provides no indication for a direct intermolecular pathway for proton movement between OH and H_2O ligands: there are no short contacts between O(1) and O(3) sites (Table 4), and while there is a strong H bond between O(1) and the water molecule O(5) (2.64(4) Å), the latter is not hydrogen bonded to O(3). The only possibility for an H^+ shuttle between the two sites would be via the $NH_3(4)$ group and would require intermediate formation of an amide species.

TABLE 4. Selected non-bonded and hydrogen bonding distances in **2**

Cl11...O5′	3.30(3)[a]
Cl12...O5′	3.26(3)[a]
Cl22...O5′	3.34(4)[b]
O1...O5	2.64(4)
O2...N2	3.14(3)[c]
O3...O3	3.20(4)[c]
O3...N2	2.89(3)[c]
O3...N4	2.74(3)[c]
O4a–N2	2.87(3)[c]
O5–N4	2.94(4)

Primed atoms are obtained from those unprimed by the symmetry operations: [a]$1+x$, $1+y$, z. [b]$1+x$, $1+y$, $1+z$. [c]$1-x$, $-y$, $1-z$.

There are two half $AuCl_4^-$ entities, each located on a crystallographic inversion centre; their coordination is square-planar with normal Au–Cl bond lengths [22].

Conclusions

The Pt(II) compound *cis*-$(NH_3)_2Pt(1\text{-MeT})_2$ reacts with $AuCl_4^-$ in aqueous solution with protonation to *cis*-$[(NH_3)_2Pt(1\text{-MeT})(1\text{-MeTH})][AuCl_4]\cdot H_2O$ (**1**) and parallel with oxidation to *cis*-$[(NH_3)_2Pt(1\text{-MeT})_2(OH)(OH_2)][AuCl_4]\cdot H_2O$ (**2**). **2** appears to be only the third structurally characterized bis(nucleobase) complex of Pt(IV) having a *cis* orientation of the two bases, the two others being Pt(IV) (cyclohexyldiamine) complexes of 9-methylguanine [23]. Previously studied bis(nucleobase) complexes of Pt(IV) containing pyrimidine bases were without exception of a *trans* geometry [18, 20].

A noteworthy detail of the formation of **2** is that the cation does not contain a Cl bound to Pt, even though Cl^- was present in solution from which the compound crystallized. We assume that this is so due to steric crowding caused by the exocyclic oxygens of 1-MeT. While in *cis,cis,trans*-$[(dach)Pt(9\text{-MeGH-}N7)_2Cl_2]^{2+}$ (dach = diaminocyclohexane, 9-MeGH = 9-methylguanine) Pt can still accommodate two axial chlorides without serious deviations from octahedral geometry [23], the situation in the bis(nucleobase) complexes containing N(3) bound pyrimidine nucleobases is much tighter. This argument probably also holds for a *trans* orientation of the two pyrimidine nucleobases, considering our failure [18b] to prepare a Cl derivative of *trans*-$[(NH_3)_2Pt(1\text{-MeC-}N3)_2(OH)(OH_2)]^+$ (1-MeC = 1-methylcytosine) via HCl treatment.

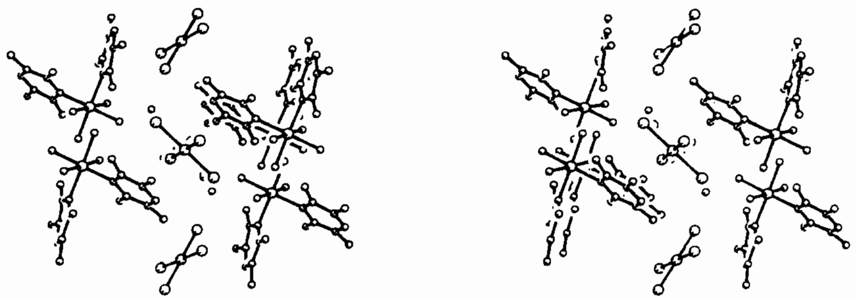


Fig. 3. Stereoscopic view of packing of the title compound.

Supplementary material

Tables of calculated and observed structure factors, calculated hydrogen positions, anisotropic displacement parameters and an extended list of bond distances, angles and torsion angles may be obtained from the authors upon request.

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