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# Au$^{III}$ binding to C5 of the model nucleobase 1,3-dimethyluracil (1,3-DimeU): Preparation and X-ray crystal structures of *trans*-K[Au(CN)$_2$Cl(1,3-DimeU$^-$)] and of two derivatives

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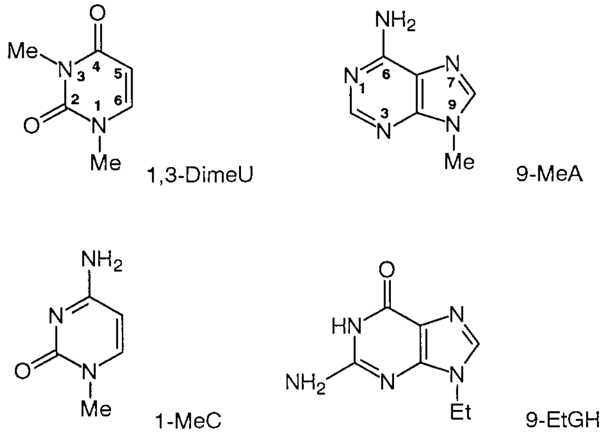
**Abstract**

The reaction of *trans*-K[Au(CN)$_2$Cl$_2$] with 1,3-dimethyluracil (1,3-DimeU) gives *trans*-K[Au(CN)$_2$Cl(1,3-DimeU$^-$–$C^5$)] (**1**) which contains the 1,3-dimethyluracil-5-yl entity (1,3-DimeU$^-$–$C^5$) bound to Au$^{III}$. Complex **1** represents the first example of an X-ray structurally characterized organogold(III) complex of a nucleobase. Further reaction with purine model nucleobases (nb) such as 9-ethylguanine (9-EtGH), 9-methyladenine (9-MeA), and 1-methylcytosine (1-MeC) leads to mixed nucleobase complexes of type *trans*-[Au(CN)$_2$(1,3-DimeU$^-$–$C^5$)(nb)] (nb = 9-MeA, **2a**; nb = 9-EtGH, **3a**; nb = 1-MeC, **4a**) or to compounds containing the protonated purine base Hnb$^+$ and [Au(CN)$_2$X(1,3-DimeU$^-$–$C^5$)]$^-$ as a counter ion (X = Cl or CN), e.g. [9-MeAH][Au(CN)$_2$Cl(1,3-DimeU$^-$–$C^5$)] · H$_2$O (**2b**) and [9-EtGH$_2$][Au(CN)$_3$(1,3-DimeU$^-$–$C^5$)] (**3b**). The crystal structures of **1**, **2b**, and **3b** were determined. The C-bound nucleobase exerts a distinct *trans*-influence, as evident from long Au–Cl bonds in **1** and **2b** (2.340(3) Å and 2.358(6) Å) and a long bond (2.082(7) Å) between Au and the cyano ligand *trans* to 1,3-DimeU$^-$ in **3b**. © 1998 Elsevier Science S.A.

*Keywords:* Gold(III); Nucleobase; Uracil; Crystal structure

## 1. Introduction

In the model nucleobase 1,3-dimethyluracil (1,3-DimeU), the N$^3$ position, which is a frequent binding site in uracil nucleobases for metal ions, is blocked and therefore unavailable (Scheme 1). Binding of light transition metal ions has been demonstrated to occur via the exocyclic O$^4$ position, however [1,2], whereas the heavy transition metal ions Hg$^{2+}$ [3–6] and Pt$^{2+}$ [4] can also bind to the C$^5$ position with displacement of an aromatic proton. This reaction may involve initial binding to O$^4$ with the metal entity in an *anti* orientation relative to N$^3$ [4]. Similarly, reaction of [AuCl$_4^-$] with this ligand takes place at C$^5$, followed by oxidative dimerization to di(1,3-dimethyluracil–$C^5$,$C^{5'}$) [7]. Although we were able to detect the C$^5$ metalated species by $^1$H NMR spectroscopy in solution and to characterize the oxidation product by X-ray crystallography, we were unable as yet to crystallize [AuCl$_3$(1,3-DimeU$^-$–



Scheme 1.

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$C^5$)]$^-$. Starting from *trans*-K[Au(CN)$_2$Cl$_2$] instead of Na[AuCl$_4$], however, we have now isolated and structurally characterized the first Au$^{III}$ complexes containing a C-bound nucleobase, *trans*-K[Au(CN)$_2$Cl(1,3-DimeU$^-$–$C^5$)] (**1**), [9-MeAH][Au(CN)$_2$Cl(1,3-DimeU$^-$–$C^5$)] (**2b**), and [9-EtGH$_2$][Au(CN)$_3$(1,3-DimeU$^-$–$C^5$)] (**3b**). In addition, the mixed nucleobase complexes *trans*-[Au(CN)$_2$(1,3-DimeU$^-$–$C^5$)(9-MeA)] (**2a**) and *trans*-[Au(CN)$_2$(1,3-DimeU$^-$–$C^5$)(9-EtGH)] (**3a**) were obtained, but due to their poor solubility in water, these complexes could not be isolated as single crystals. The described compounds extend the short list of X-ray structurally characterized examples of Au$^{III}$ nucleobase coordination compounds [8–11].

## 2. Experimental details

### 2.1. Preparations

*trans*-K[Au(CN)$_2$Cl$_2$] [12], 9-methyladenine (9-MeA) [13], and 8-deutero-9-methyladenine [14] were prepared as previously described; 1,3-dimethyluracil (1,3-DimeU) and 9-ethylguanine (9-EtGH) were of commercial sources.

*trans*-K[Au(CN)$_2$Cl(1,3-DimeU$^-$–$C^5$)] (**1**). K[Au(CN)$_2$Cl$_2$] (0.3 mmol in 6 cm$^3$ water) and 1,3-DimeU (0.3 mmol) were mixed and the solution (pH 1.9) allowed to react for 20 d at 25°C. The yellow solid that had formed (AuCN; $\nu$CN 2231 cm$^{-1}$) was filtered off and the filtrate was then cooled to 4°C. Colorless crystals that formed were filtered off and dried in air (20%). (Found: C, 20.9; H, 1.4; N, 12.2. Calc. for $C_8H_7N_4O_2ClKAu$: C, 20.8; H, 1.3; N, 12.1).

*trans*-[Au(CN)$_2$(1,3-DimeU$^-$–$C^5$)(9-MeA)] · 3H$_2$O (**2a**). Complex **1** (0.3 mmol in 2 cm$^3$ water) was mixed with 9-MeA (0.3 mmol) and the pH of the solution was adjusted to ca. 4 with HNO$_3$ (1 N). The solid that formed was filtered off, washed with water, and dried in air (47%). (Found: C, 28.7; H, 3.4; N, 21.5. Calc for $C_{14}H_{20}N_9O_5Au$: C, 28.4; H, 3.4; N, 21.3).

[9-MeAH][Au(CN)$_2$Cl(1,3-DimeU$^-$–$C^5$)] · H$_2$O (**2b**). Compound **2b** was prepared by reacting **1** (0.1 mmol in 1 cm$^3$ water) with 9-MeA (0.1 mmol) at pH ca. 1 (adjusted with 1 M HCl). The solution obtained was left at 25°C overnight. The colorless crystals that had formed were filtered off and dried in air (82%). (Found: C, 28.8; H, 2.9; N, 21.7. Calc for $C_{14}H_{17}N_9O_3ClAu$: C, 28.4; H, 2.9; N, 21.3).

*trans*-[Au(CN)$_2$(1,3-DimeU$^-$–$C^5$)(9-EtGH)] · H$_2$O (**3a**) and [9-EtGH$_2$][Au(CN)$_3$(1,3-DimeU$^-$–$C^5$)] (**3b**). Complex **3a** was obtained by the method used for **2a** (62%), however, with 9-EtGH instead of 9-MeA. (Found: C, 31.1; H, 2.9; N, 22.0. Calc for $C_{15}H_{18}N_9O_4Au$: C, 30.8; H, 3.1; N, 21.5). After filtration of **3a**, the solution was cooled at 4°C overnight. The crystals of **3b** that had formed were then filtered off and dried in air (11%). (Found: C, 31.2; H, 2.8; N, 22.3.

Table 1
Summary of crystal data, data collection parameters and refinements of compounds **1**, **2b**, and **3b**

| | **1** | **2b** | **3b** |
|---|---|---|---|
| Formula | $C_8H_7AuKClO_2N_4$ | $C_{14}H_{17}AuClO_3N_9$ | $C_{16}H_{17}AuO_3N_{10}$ |
| $M$ | 462.69 | 591.77 | 594.35 |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic |
| Space group | $Pna2_1$ | $P2_1/n$ | $P2_1/n$ |
| $a$ (Å) | 14.068(7) | 7.155(3) | 9.852(4) |
| $b$ (Å) | 11.199(4) | 15.129(4) | 7.9068(7) |
| $c$ (Å) | 7.720(2) | 17.671(8) | 25.81(1) |
| $\beta$ (°) | | 91.21(2) | 98.13(2) |
| $U$ (Å$^3$) | 1216.3(8) | 1912(1) | 1990(1) |
| $D_{calc}$ (g cm$^{-3}$) | 2.53 | 2.06 | 1.98 |
| $Z$ | 4 | 4 | 4 |
| $\mu$ (MoK $\alpha$) (cm$^{-1}$) | 126.33 | 78.55 | 74.19 |
| $F$(000) | 856 | 1136 | 1144 |
| $2\theta_{max}$ (°) | 60 | 54 | 56 |
| Octants collected | $+h, +k, +l$ | $\pm h, +k, +l$ | $\pm h, +k, +l$ |
| Number of measured reflections | 2054 | 4475 | 5245 |
| % Transmitted min, max | 75.5, 100 | 92.1, 99.9 | 62.2, 99.9 |
| Number of independent reflections [$I \geq 3\sigma(I)$] | 1408 | 2119 | 3837 |
| Number of variables | 153 | 254 | 271 |
| $R$ ($F_o$) | 0.026 | 0.043 | 0.041 |
| $Rw$ ($F_o$) | 0.029 | 0.049 | 0.048 |
| Goodness of fit | 1.37 | 1.25 | 1.53 |
| Residuals (e Å$^{-3}$) | 0.97, −1.10 | 1.46, −1.20 | 1.64, −1.77 |

Calc for $C_{16}H_{17}N_{10}O_3Au$: C, 32.33; H, 2.89; N, 23.57). Elemental analysis data are in better agreement if presence of one molecule of $H_2O$ is assumed: C, 31.38; H, 3.13; N, 22.88.

*trans*-[Au(CN)$_2$(1,3-DimeU$^-$–*C*$^5$)(1-MeC)] (**4a**). The compound was prepared on a NMR scale only and identified by $^1$H NMR spectroscopy.

1,3-Dimethyl-5-cyanouracil(1,3-Dime-5–CN–U) (**5**) was identified by mass spectrometry of an aged reaction mixture of **1** and 1,3-DimeU in $D_2O$ (cf. text). According to $^1$H NMR spectroscopy, the solution contained a single species: $\delta$ 8.45(1H, s), 3,48(3H, s), 3.31(3H, s). MS: $m/z$ 165.1.

### 2.2. Instrumentation

Chemical analyses were performed by the University of Dortmund Microanalytical Laboratory. IR spectra (KBr pellets) were recorded on a Bruker IFS 113 v spectrometer. $^1$H NMR (200.13 MHz) were measured on a Bruker AC200 instrument. Chemical shifts are given in ppm and are referenced to internal TSP ($D_2O$) and TMS (DMSO-$d_6$). pH$^*$ denotes uncorrected pH values taken from $D_2O$ solutions. The mass spectrum of **5** was recorded on a WG Autospec instrument in $D_2O$ under EI$^+$ conditions.

### 2.3. X-ray crystallography

Suitable crystals for X-ray investigation of compounds **1**, **2b**, and **3b** were obtained according to the above procedures. Details of crystal parameters, data collection and refinements are summarized in Table 1.

Table 2
Atomic coordinates of non-hydrogen atoms of **1**

| Atom | x | y | z | B (Å$^2$) |
|---|---|---|---|---|
| Au | 0.22860(2) | 0.25870(3) | 0.500 | 2.033(5) |
| K | 0.0487(2) | 0.0459(2) | 0.0676(4) | 2.77(5) |
| Cl | 0.1914(3) | 0.4618(2) | 0.5224(8) | 4.30(7) |
| O2 | 0.3531(7) | −0.2522(8) | 0.593(1) | 4.2(2) |
| O4 | 0.1285(6) | 0.0042(8) | 0.385(1) | 2.9(2) |
| N1 | 0.3861(7) | −0.0561(8) | 0.597(2) | 2.7(2) |
| N3 | 0.2444(6) | −0.1229(7) | 0.478(1) | 2.5(2) |
| N7 | 0.046(1) | 0.187(1) | 0.711(2) | 5.1(3) |
| N8 | 0.4143(7) | 0.344(1) | 0.309(2) | 3.0(2) |
| C1 | 0.477(1) | −0.081(2) | 0.682(3) | 5.0(4) |
| C2 | 0.3292(8) | −0.1521(9) | 0.559(2) | 2.8(2) |
| C3 | 0.180(1) | −0.224(1) | 0.425(2) | 3.7(3) |
| C4 | 0.2074(8) | −0.0088(9) | 0.448(1) | 2.1(2) |
| C5 | 0.2717(7) | 0.0847(7) | 0.509(3) | 2.5(1) |
| C6 | 0.3571(7) | 0.0599(9) | 0.569(2) | 2.4(2) |
| C7 | 0.1104(9) | 0.213(1) | 0.631(2) | 2.9(2) |
| C8 | 0.3488(9) | 0.310(1) | 0.374(2) | 2.4(2) |

Isotropic equivalent displacement parameter defined as: $(4/3)\Sigma_i\Sigma_j a_i a_j B(i,j)$.

Table 3
Atomic coordinates of non-hydrogen atoms of **2b**

| Atom | x | y | z | B (Å$^2$) |
|---|---|---|---|---|
| Au | 0.12320(8) | 0.14680(4) | 0.21551(3) | 3.109(8) |
| Cl | 0.2093(8) | 0.2643(4) | 0.2967(3) | 7.4(1) |
| O2 | −0.069(2) | −0.1917(7) | 0.0512(7) | 5.0(3) |
| O4 | 0.311(2) | 0.0459(7) | 0.0717(6) | 4.9(3) |
| N1 | −0.151(2) | −0.0818(9) | 0.1297(8) | 4.8(3) |
| N3 | 0.124(2) | −0.0699(9) | 0.0602(7) | 3.8(3) |
| N7 | −0.254(2) | 0.236(1) | 0.1669(9) | 5.0(3) |
| N8 | 0.495(2) | 0.058(1) | 0.2645(9) | 5.4(4) |
| C1 | −0.323(3) | −0.128(2) | 0.152(1) | 7.4(5) |
| C2 | −0.034(2) | −0.120(1) | 0.0793(9) | 4.4(4) |
| C3 | 0.243(2) | −0.109(1) | 0.009(1) | 5.1(4) |
| C4 | 0.170(2) | 0.009(1) | 0.093(1) | 4.2(4) |
| C5 | 0.051(2) | 0.040(1) | 0.1528(9) | 3.9(3) |
| C6 | −0.103(2) | −0.007(1) | 0.167(1) | 4.5(4) |
| C7 | −0.115(2) | 0.205(1) | 0.1873(9) | 3.6(3) |
| C8 | 0.363(2) | 0.089(1) | 0.2457(9) | 4.2(3) |
| N1a | −0.008(2) | 0.1597(7) | 0.4726(6) | 3.2(2) |
| N3a | 0.267(2) | 0.0693(8) | 0.4688(7) | 3.8(3) |
| N6a | −0.279(2) | 0.1376(9) | 0.4007(8) | 4.7(3) |
| N7a | −0.074(2) | −0.0242(9) | 0.3414(8) | 4.3(3) |
| N9a | 0.217(2) | −0.0538(8) | 0.3818(7) | 3.3(2) |
| C2a | 0.171(2) | 0.136(1) | 0.493(1) | 4.7(4) |
| C4a | 0.162(2) | 0.023(1) | 0.4187(9) | 3.4(3) |
| C5a | −0.018(2) | 0.0390(9) | 0.3918(8) | 3.0(3) |
| C6a | −0.107(2) | 0.112(1) | 0.4186(9) | 3.5(3) |
| C8a | 0.070(2) | −0.078(1) | 0.3379(9) | 4.1(3) |
| C9a | 0.394(2) | −0.096(1) | 0.390(1) | 4.8(4) |
| Ow | 0.398(2) | 0.2230(7) | 0.0792(6) | 4.7(3) |

Isotropic equivalent displacement parameter defined as: $(4/3)\Sigma_i\Sigma_j a_i a_j B(i,j)$.

Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with graphite monochromator and MoK$\alpha$ radiation ($\lambda = 0.71069$ Å). Intensities of three standard reflections, measured during data collections, did not show any decay for all compounds. Reflections having intensities $I > 3\sigma(I)$ were corrected for Lorentz-polarization factors and used in subsequent refinements. An absorption correction, based on empirical $\psi$-scan, was applied to all data.

Structures were determined by conventional Patterson method and subsequent Fourier syntheses. The final refinements on $F_o$ were carried out with anisotropically thermal parameters for all non-H atoms. Hydrogen atoms at calculated positions (C–H bond distance 0.95 Å) were introduced in final cycles of refinements as fixed contribution ($B = 1.3 \times B$eq of their bonded atom). The final weighting scheme was unit for all the compounds.

The refinement of the enantiomer of **1** gave $R = 0.029$ and $Rw = 0.032$, confirming the correct assignment of the absolute configuration for this structure.

Atomic scattering factors and anomalous dispersion parameters were taken from Ref. [15]. All calculations were carried out on a $\mu$-VAX2000 computer using the Enraf-Nonius MolEN package [16]. Final atomic coor-

Table 4
Atomic coordinates of non-hydrogen atoms of **3b**

| Atom | x | y | z | B (Å$^2$) |
|---|---|---|---|---|
| Au | 0.09384(3) | 0.07025(4) | 0.21590(1) | 2.438(5) |
| O2 | 0.6408(6) | 0.030(1) | 0.3570(3) | 3.6(1) |
| O4 | 0.1848(6) | −0.080(1) | 0.3305(3) | 3.8(1) |
| N1 | 0.5195(7) | 0.104(1) | 0.2816(3) | 2.9(1) |
| N3 | 0.4102(7) | −0.018(1) | 0.3447(3) | 2.6(1) |
| C1 | 0.6443(9) | 0.162(2) | 0.2603(5) | 4.9(3) |
| C2 | 0.5301(8) | 0.039(1) | 0.3289(3) | 2.8(2) |
| C3 | 0.418(1) | −0.085(2) | 0.3980(4) | 4.0(2) |
| C4 | 0.2833(8) | −0.016(1) | 0.3139(3) | 2.5(1) |
| C5 | 0.2780(7) | 0.058(1) | 0.2643(2) | 1.9(1) |
| C6 | 0.3959(8) | 0.114(1) | 0.2462(4) | 3.4(2) |
| C7 | 0.1796(9) | −0.047(1) | 0.1611(3) | 3.5(2) |
| N7 | 0.2312(9) | −0.111(1) | 0.1289(4) | 5.0(2) |
| C8 | 0.0154(8) | 0.195(1) | 0.2716(3) | 3.0(2) |
| N8 | −0.0309(8) | 0.269(1) | 0.3026(3) | 3.9(2) |
| C9 | −0.0939(8) | 0.079(1) | 0.1675(2) | 2.3(1) |
| N9 | −0.189(1) | 0.079(1) | 0.1460(4) | 5.4(2) |
| O6a | 0.3203(6) | 0.169(1) | 0.4949(3) | 4.4(2) |
| N1a | 0.1834(7) | 0.127(1) | 0.5582(3) | 2.9(1) |
| N2a | 0.0612(8) | 0.074(1) | 0.6255(3) | 4.4(2) |
| N3a | −0.0523(7) | 0.197(1) | 0.5508(3) | 4.0(2) |
| N7a | 0.0543(8) | 0.311(1) | 0.4310(3) | 3.7(2) |
| N9a | −0.1308(8) | 0.318(2) | 0.4666(4) | 5.9(2) |
| C2a | 0.0616(8) | 0.134(1) | 0.5773(3) | 3.0(2) |
| C4a | −0.0331(8) | 0.248(1) | 0.5030(4) | 3.5(2) |
| C5a | 0.0841(8) | 0.245(1) | 0.4805(3) | 2.9(2) |
| C6a | 0.2074(9) | 0.179(1) | 0.5086(4) | 3.1(2) |
| C8a | −0.076(1) | 0.354(2) | 0.4233(4) | 5.3(3) |
| C9a | −0.269(2) | 0.386(3) | 0.4799(7) | 11.9(6) |
| C10a | −0.358(3) | 0.259(3) | 0.4670(9) | 11.7(7) |

Isotropic equivalent displacement parameter defined as: $(4/3) \sum_i \sum_j a_i a_j B(i,j)$.

dinates and equivalent isotropic thermal parameters are given in Tables 2–4. Further details on the crystal structure analyses may be obtained from E.Z. on request.

## 3. Results and discussion

### 3.1. Formation of complexes

### 3.1.1. Formation of 1

When the reaction between *trans*-K[Au(CN)$_2$Cl$_2$] and 1,3-DimeU is followed by $^1$H NMR spectroscopy (pH$^*$ 1.9, D$_2$O, 1:1 ratio), formation of several water soluble compounds is observed. Within 1 day of reaction (Fig. 1a) a new singlet at $\delta$ 7.51, upfield shifted from the H(6) doublet of 1,3-DimeU, is observed. This new resonance is assigned to H(6) of the 1,3-DimeU$^-$ ligand of compound **1**. The chemical shift of this resonance is in agreement with similar Au–C(uracil) compounds observed before [7]. Within ca. 20 days of reaction (Fig. 1a–d) compound **1** represents the main product. At this stage, another singlet at $\delta$ 8.45 due to **5** is observed, which is of low intensity, and formation of a yellow insoluble solid, identified by IR and elemental analysis as AuCN, has occurred. With very long reaction times (ca. 3 months, pH$^*$ 1.4) **5** remains as the only species in solution. By then, more AuCN has precipitated. The new compound **5** was identified at that point by mass spectrometry as 1,3-Dime-5–CN–U. Its formation appears to be analogous to that of 1,3-dimethyl-5-chlorouracil from AuCl$_4^-$ and 1,3-DimeU [7].

The minor resonance at $\delta$ 7.38 most likely is due to a Cl$^-$ hydrolysis product of **1**, hence *trans*-[Au(CN)$_2$(1,3-DimeU$^-$–*C*$^5$)(OD$_2$)] / *trans*-[Au(CN)$_2$(1,3-DimeU$^-$–*C*$^5$)(OD)]$^-$, since its intensity increases at the expense of the $\delta$ 7.51 resonance with AgNO$_3$ added.

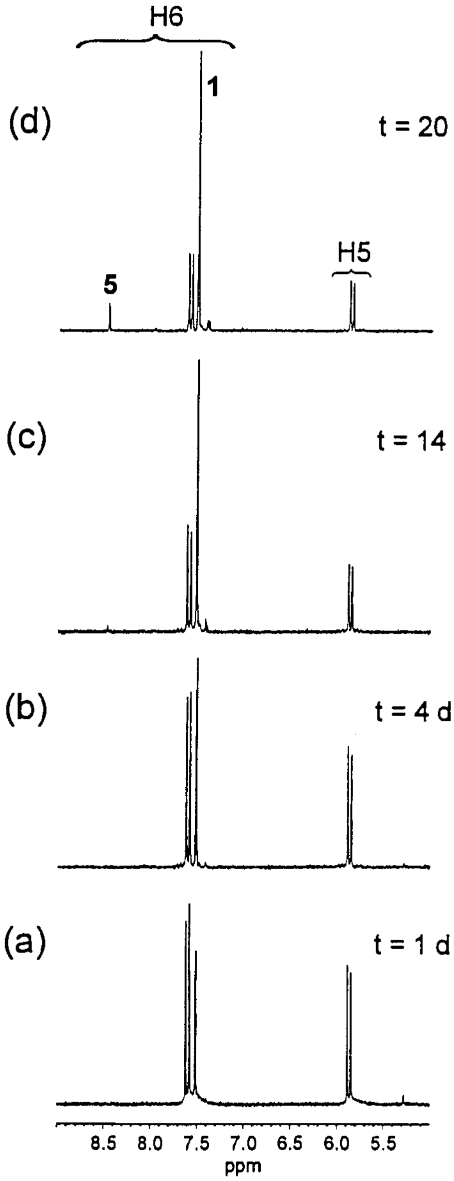

Fig. 1. Reaction between *trans*-K[Au(CN)$_2$Cl$_2$] and 1,3-DimeU as followed by $^1$H NMR spectroscopy (low field section only; D$_2$O; pH$^*$ 1.9).

Complex **1** was isolated in crystalline form on a preparative scale and characterized by X-ray analysis (vide infra). As compared to free 1,3-DimeU, the IR spectrum of **1** shows the most significant changes in the bands due to $\nu$(C=O) and $\nu$(C=C): relative to the free base, these very intense bands are shifted to lower energies (1692 and 1623 $cm^{-1}$). The two intense and sharp bands at 755 and 815 $cm^{-1}$ of 1,3-DimeU are replaced by a weaker band at 766 $cm^{-1}$. The weak absorption at 2170 $cm^{-1}$ is assigned to $\nu$(C≡N). The changes observed for the uracil modes are very similar to those described previously for mercury binding to $C^5$ of 1,3-$DimeU^-$ [4].

### 3.1.2. Reaction of **1** with 9-MeA

Reaction of **1** with 9-MeA ($H_2O$, pH 4–5, 1:1 ratio) gives the neutral complex *trans*-[$Au(CN)_2$(1,3-$DimeU^-$–$C^5$)(9-MeA)] **2a**. This compound is not water soluble but dissolves in DMSO and DMF. The $^1H$ NMR spectrum of **2a** (DMSO-$d_6$) displays a singlet due to H(6) of 1,3-$DimeU^-$ at $\delta$ 7.46 and a relatively broad resonance at $\delta$ 8.37. The latter is assigned to both H(2) and H(8) of 9-MeA, since upon use of 8-deuterated 9-MeA, the integral of this signal decreases by 50%. A third signal, at $\delta$ 8.90, disappears after addition of $D_2O$, and is therefore assigned to the amino group of the 9-MeA. The large downfield shift of this resonance relative to the free ligand 9-MeA in the same solvent [$\delta$ 7.19] is consistent with N(6)–H...O(4) hydrogen bonding between 9-MeA and 1,3-$DimeU^-$, as previously seen in mixed thymine,adenine complexes [17,18]. Since only the $N^7$ linkage isomer is capable of forming this intramolecular H bond, yet not the $N^1$ linkage isomer, $Au^{III}$ coordination to the adenine nucleobase must be through $N^7$.

If the reaction is carried out at a pH below ca. 1 (HCl, 1 M), protonation of 9-MeA and/or excess $Cl^-$ prevents binding of $Au^{III}$ and instead crystals of [9-MeAH][$Au(CN)_2Cl$(1,3-$DimeU^-$–$C^5$)] **2b** are formed in quantitative yield. The $^1H$ NMR spectrum of **2b** ($D_2O$, pD 1.2) is consistent with the presence of protonated 9-MeA.

### 3.1.3. Reaction of **1** with 9-EtGH

Upon reaction of **1** with 9-EtGH ($H_2O$, pH 4–5, 1:1 ratio) the neutral compound *trans*-[$Au(CN)_2$(1,3-Di-$meU^-$–$C^5$)(9-EtGH)] **3a** is formed. According to $^1H$ NMR spectroscopy (DMSO-$d_6$), 1,3-DimeU and 9-EtGH are present in **3a** in a 1:1-ratio. Gold binding to $N^7$ of 9-EtGH is concluded from a considerable downfield shift of the H(8) guanine resonance (+1.0 ppm) relative to free 9-EtGH and the presence of N(1)H at $\delta$ 11.32 and of the $N(2)H_2$ resonance at $\delta$ 6.95. The signal at $\delta$ 7.43 is assigned to H(6) of 1,3-$DimeU^-$. We have previously isolated a related mercury compound with this coordination pattern [5].

After isolation of **3a**, a second species was obtained in low yield from the filtrate and characterized by X-ray analysis as [9-$EtGH_2$][$Au(CN)_3$(1,3-$DimeU^-$–$C^5$)] **3b**. The $^1H$ NMR spectrum of this compound ($D_2O$, $pH^*$ 0.8) shows signals corresponding to protonated 9-ethylguanine, [9-$EtGH_2$]$^+$, and H(6) of 1,3-$DimeU^-$ in the expected range ($\delta$ 7.58, s). Formation of **3b** cannot be rationalized at present. We rule out the possibility that the starting compound K[$Au(CN)_2Cl_2$] was contaminated with K[$Au(CN)_3Cl$], however, considering the simplicity of the IR spectrum of the starting material **1** (single, sharp absorption at 2189 $cm^{-1}$).

### 3.1.4. Reaction of **1** with 1-MeC

The addition of 1-MeC to a solution of **1** ($D_2O$, $pH^*$ 4–5, 1:1 ratio) leads to the formation of the neutral complex *trans*-[$Au(CN)_2$(1,3-$DimeU^-$)(1-MeC)] **4a**. The $^1H$ NMR spectrum of **4a** (DMSO-$d_6$) shows resonances at $\delta$ 8.83 and $\delta$ 8.63 corresponding to exchangeable protons of the amino group of 1-MeC and doublets due to H6 ($\delta$ 7.93, $^3J$ 7.5 Hz) and H5 ($\delta$ 6.04) of 1-MeC. The H(6) resonances of the 1,3-$DimeU^-$ ligand is normal ($\delta$ 7.39, s). The three *N*-methyl resonances of the two ligands occur between $\delta$ 3.21 and $\delta$ 3.39. The 1-MeC resonances are consistent with $N^3$ metal binding.

No reaction was observed between **1** and 1-methylthymine (1:1, $D_2O$, $pH^*$ 2–9). Considering our previous findings of $N^3$ metalated $Au^{III}$ complexes of uracil and thymine ligands [9,11], this result was unexpected.

## 3.2. Crystal structures

### 3.2.1. trans-K[$Au(CN)_2Cl$(1,3-$DimeU^-$–$C^5$)] (**1**)

The crystal is built up by [$Au(CN)_2Cl$(1,3-$DimeU^-$–$C^5$)]$^-$ anions and $K^+$ cations. The ORTEP [19] drawing of the anion, together with the atom numbering scheme is shown in Fig. 2. Coordination bond lengths and angles for this and other structures are given in Table 5.

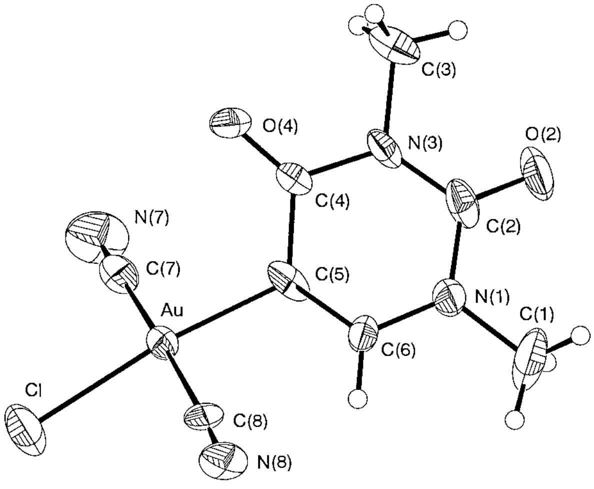

Fig. 2. An ORTEP drawing and atom numbering scheme of the anion of **1** (50% probability thermal ellipsoids).

Table 5
Coordination bond lengths (Å) and angles (°) and dihedral angles $\alpha$ (°) between the coordination and the 1,3-DimeU$^-$ plane

| | 1 | 2b | 3b |
|---|---|---|---|
| Au–X | 2.340(3) | 2.358(6) | 2.082(7) |
| Au–C(5) | 2.042(8) | 2.02(2) | 2.053(6) |
| Au–C(7) | 2.01(1) | 1.97(1) | 1.98(1) |
| Au–C(8) | 2.04(1) | 1.99(2) | 1.989(9) |
| X–Au–C(5) | 172.4(6) | 175.6(5) | 179.2(3) |
| X–Au–C(7) | 91.4(4) | 91.9(5) | 91.2(3) |
| X–Au–C(8) | 86.8(3) | 87.5(5) | 90.8(3) |
| C(5)–Au–C(7) | 89.2(5) | 90.5(6) | 89.0(3) |
| C(5)–Au–C(8) | 92.4(5) | 90.1(6) | 89.1(3) |
| C(7)–Au–C(8) | 177.8(5) | 179.1(7) | 177.2(3) |
| $\alpha$ | 53.6(3) | 57.8(4) | 53.9(2) |

(X = Cl in **1** and **2b**, = C(9) in **3b**).

Au$^{III}$ is bound to the nucleobase through C$^5$ and the square planar coordination is completed by Cl, *trans* to C$^5$, and two *trans* cyano groups. The coordination geometry about Au$^{III}$ presents a slightly tetrahedral distortion: C(5) and Cl are displaced by +0.06 Å and C(7) and C(8) by −0.06 Å out of their mean plane, whereas Au is displaced by +0.085 Å. The 1,3-DimeU$^-$ ligand is planar within ±0.04 Å and its mean plane makes a dihedral angle, $\alpha$, of 53.7(3)° with the mean coordination plane. The Au–C(5) and the mean Au–CN distances are 2.042(8) and 2.03(1) Å, respectively. The Au–Cl distance of 2.340(3) Å is significantly longer than the mean value of 2.280(2) Å reported in $[AuCl_4]^-$ [20] and than those of about 2.270 Å, reported in Au$^{III}$ complexes having weak *trans*-influencing donors, such as Cl and N [21–23]. The comparison indicates the strong *trans*-influence exerted by the C-bound uracil ligand. Recently, new complexes of the type $[Au^{III}Cl_2L]$, where L is a chelate ligand consisting of a phenyl group C-bonded to Au and bearing a N-donor substituent such as oxazoline and/or dimethylaminomethyl, have been reported [24]. In these complexes, the Au–Cl distances, *trans* to a C-sp$^2$ atom, vary from 2.353(3) to 2.369(3) Å and do not differ significantly from that here reported. This effect has been also observed in Pt$^{II}$ complexes where Cl is *trans* to a 1,3-DimeU$^-$–*C*$^5$ [4]. In fact, in the latter, the Pt–Cl distance is found to be 2.40(1) Å, significantly longer than the mean values of 2.304(4) Å of the two *trans* Pt–Cl distances in $[PtCl_3(9\text{-}MeGH_2)]$ (9-MeGH$_2$ = 9-methylguaninium) [25].

The internal bond lengths and angles in 1,3-DimeU$^-$ reflects, within the experimental errors, the trend reported for uracil and thymine in a statistical survey of nucleobases [26]. The influence of the bonding through C$^5$ on the geometry of the ligand, if any, cannot be detected (see structure **3b**).

The K$^+$ ion has seven nearest neighbors with distances varying from 2.658(9) to 3.17(1) Å, making a very distorted pentagonal bipyramid. Three coordinating oxygens pertain to carboxyl and four nitrogen atoms to cyano groups of different complex units.

### 3.2.2. *trans-[Au(CN)$_2$Cl(1,3-DimeU$^-$–C$^5$)][9-MeAH]·H$_2$O* (**2b**)

The crystal contains [Au(CN)$_2$Cl(1,3-DimeU$^-$–*C*$^5$)]$^-$ anions, 9-MeAH cations and crystallization water molecules. Fig. 3 provides the molecular structures of the ions, together with the labelling scheme. The geometry of the anion is very similar to that of **1**, within the experimental errors (Table 5). The 1,3-DimeU$^-$ ring, planar within ±0.05 Å, makes an angle of 57.8(4)° with the mean coordination plane. The protonated purine base is planar within ±0.02(2) Å. The recent statistical analysis of the geometries of neutral and N1 protonated adenine [24] indicates that on protonation the main geometrical variations between the two species consist in a lengthening of the N(1)–C(2) distance, a shortening of the C(2)–N(3) bond as well as in a widening of the C(2)–N(1)–C(6) angle and a narrowing of the other angles involving N(1). Within the limits of the accuracy reached in the refinement of **2b**, the geometry of the cation seems to be closer to that reported for the protonated form in most respects.

A network of H bonds involves the anions, cations and water molecules. Specifically, the H bond between O(2) and N(6a) of the unit at $-0.5-x$, $-0.5+y$, $0.5-z$ is 2.94 (2) Å, whereas Ow makes four contacts, two short with N(1a) at $0.5+x$, $0.5-y$, $-0.5+z$ (2.68(2) Å) and O4 (2.75(2) Å) and two long, with N(7) at $1+x$, $+y$, $+z$ (2.91(2) Å) and O(2) at $-x$, $-y$, $-z$ (2.94(2) Å).

### 3.2.3. *[Au(CN)$_3$(1,3-DimeU$^-$–C$^5$)][9-EtGH$_2$]* (**3b**)

Crystals of **3b** contain [Au(CN)$_3$(1,3-DimeU$^-$–*C*$^5$)]$^-$ anions and protonated 9-EtGH$_2$ bases. A perspective view of the compound, together with the atom numbering scheme is shown in Fig. 4. The Au$^{III}$ coordination geometry is essentially square planar, the four donor carbon atoms being coplanar within ±0.02 Å, while Au is displaced by 0.01 Å from their mean plane. The 1,3-DimeU$^-$ ligand, planar within ±0.02 Å, makes a dihedral angle of 53.9(2)° with the coordination plane. The geometry of this ligand appears to be determined with a better accuracy than those of **1** and **2b**. Comparison of internal bond lengths and angles with the corresponding average values reported by Clowney et al. [26] for the neutral 1,3-DimeU suggests that significant variations are a lengthening of N(1)–C(6) (0.05 Å) and of C(5)–C(6) (0.04 Å) distances and a shortening of the N(1)–C(2) (0.06 Å) one, with respect to the neutral form. Correspondingly, a narrowing of the C(1)–N(1)–C(6) (5.9°) and of N(1)–C(6)–C(5) (6.7°) angles and a widening of the C(2)–N(1)–C(6) (3.5°) one are ob-

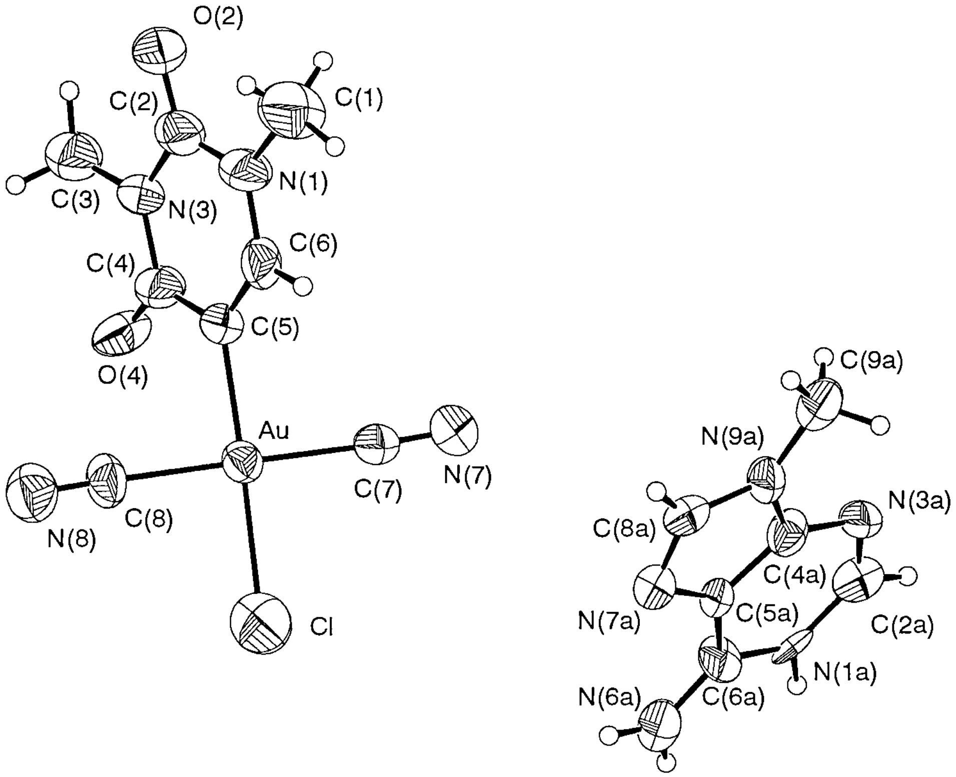

Fig. 3. An ORTEP drawing and atom numbering scheme of complex anion and 9-MeAH cation of **2b**.

served. The Au–C(5) distance of 2.053(6) Å is not significantly different from those found in **1** and **2b** (Table 5). The values of the two *cis* Au–CN distances of 1.98(1) and 1.899(9) Å are very similar and close to the mean values of 1.98(2) and 2.03(1) Å found in **1** and **2b**, respectively, and do not differ significantly from the mean value of 2.007(7) Å found in the $[Au(CN)_4]^-$ anion [27]. The Au–CN bond length, *trans*

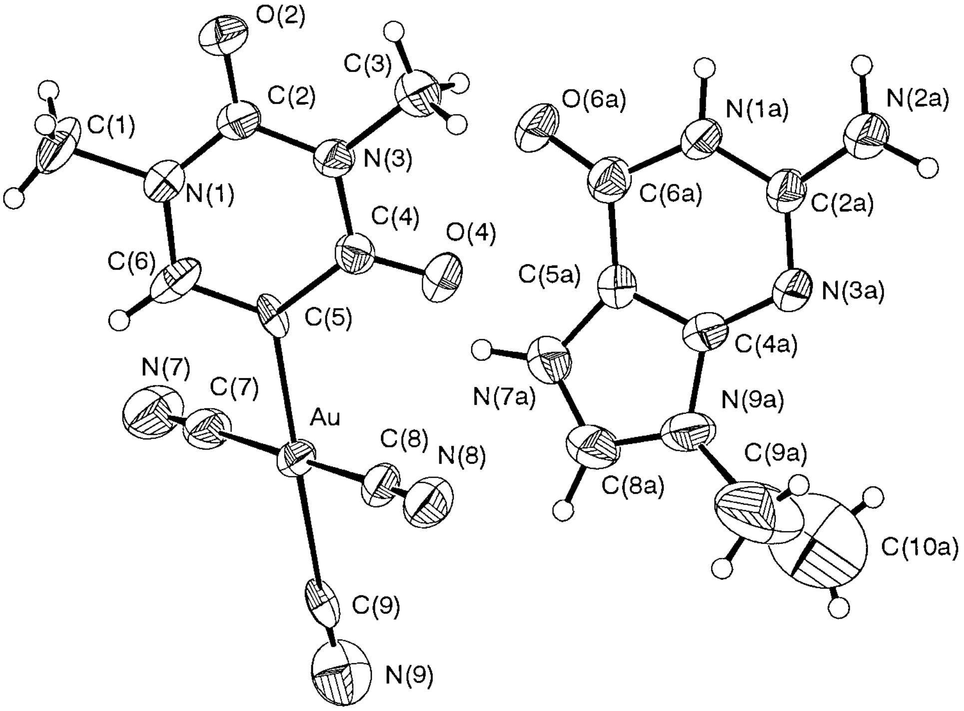

Fig. 4. An ORTEP drawing and atom numbering scheme of compound **3b**.

to $C^5$, is 2.082(7) Å and its lengthening confirms the strong *trans* influence exerted by the $\sigma$-bonded $C^5$. It is worthwhile to note that the C(9)–N(9) bond distance of 1.02(1) Å appears significantly shorter than the C(7)–N(7) and C(8)–N(8) distances, being 1.15(1) and 1.14(1) Å, respectively, and than those found in **1** and **2b**, which range from 1.10(2) to 1.15(1) Å. Analogously, in the anion $[Au(CN)_4]^-$ [27], the mean bond length is 1.126(9) Å. Unfortunately, we were not able to find in the literature accurate structural determinations of square planar complexes, containing cyano groups *trans* to a $\sigma$-bonded C atom. The observation that a lengthening of the Au–CN bond leads to a simultaneous shortening of the C–N one is in agreement with expectations.

The internal bond lengths and angles of the 9-EtGH$_2$ cation agree, within the experimental errors, with the mean values reported by Taylor and Kennard [28] as well as with those reported for $[AuCl_4][9\text{-EtGH}_2]$ [20].

A network of H bonds, based on O(2)...N(1a) $(1-x, -y, 1-z)$, O(4)...N(2a) $(-x, -y, 1-z)$ and N(7)...N(7a) $(0.5-x, -0.5+y, -0.5-z)$ contacts of 2.875(9), 2.82(1) and 2.86(1) Å, respectively, connects the anions and cations. The latter H bond is a further support to the N(7a) protonation in the free base.

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