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The Molecular Structures of Au(2,2′-bpy)$Cl_3 \cdot 2.25H_2O$ and its 1-Methyluracil Adduct [Au(2,2′-bpy)(1-MeU)$_2$]$ClO_4 \cdot 4H_2O$

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Abstract

The molecular structures and spectroscopic data (IR, ^{1}H NMR) of two Au(III) complexes are reported, Au(2,2′-bpy)$Cl_3 \cdot 2.25H_2O$ (**1**) and [Au(2,2′-bpy)(1-MeU)$_2$]$ClO_4 \cdot 4H_2O$ (**2b**) (1-MeU = 1-methyluracil anion, $C_5H_5N_2O_2$). **1** crystallizes in the space group *C*2/*c* with a = 35.452(3), b = 7.701(1), c = 22.115(2) Å, β = 90.67(1)°, V = 6037.3 Å^3, Z = 16. **2b** crystallizes in the space group *P*1 with a = 7.930(1), b = 12.606(1), c = 13.768(1) Å, α = 93.46(1)°, β = 102.62(1)°, γ = 96.74(1)°, V = 1328.5 Å^3, Z = 2. **1** is best described as consisting of dinuclear units, built up from two planar (2,2′-bpy)$AuCl_2$ entities that are connected via a long Au–Cl–Au bridge of 3.218(3) Å (Au–Cl, av.). The 2,2′-bpy rings are almost parallel and within the dinuclear unit *c.* 6.26 Å (av.) apart. **1** reacts with AgX and excess 1-MeU to give [Au(2,2′-bpy)(1-MeU)$_2$]X·$n$$H_2O$ (**2**). In **2b** (X = ClO_4^-, n = 4), the arrangement of the two 1-MeU ligands in the solid state is head-to tail, but ^{1}H NMR suggests that in aqueous solution this rotamer coexists with the head-to-head species. Comparison of **2b** with the corresponding Pt(II) and Pd(II) complexes reveals that, in its effect on the 1-MeU ring (internal ring angle at N3, IR spectrum, basicity of exocyclic oxygen, donor properties toward heterometals), the Au(III) electrophile behaves very much different and in this respect is close to the effect of a H^+. Both in strongly acidic and strongly alkaline solution, 1-MeU is displaced from **2** to give [(2,2′-bpy)Au(1-MeU)(H_2O)]$^{2+}$ (**5**) and [(2,2′-bpy)Au(1-MeU)(OH)]$^+$ (**5′**), respectively.

Introduction

Unlike their Pt(II) analogues, Au(III) complexes display a pronounced tendency to form five- and six-coordinate species [1]. Among the crystallographically characterized examples of complexes containing N donors, five-coordinate species with a square-pyramidal coordination geometry include (*o*-phen)AuX_3 [2, 3], (bq)AuX_3 [4] (bq = 2,2′-biquinoline) and (tpp)AuX [5] (tpp = tetraphenylporphinate) with X = halogen and/or CN^-, for example. Interactions between Au(III) and axial ligands (Cl and/or O) in a tetragonally elongated octahedral geometry are usually weaker, examples being [(dien)AuCl]Cl_2 and [(dien)AuCl]Cl(ClO_4) [6] and [(terpy)AuCl]$Cl_2 \cdot 3H_2O$ [7].

The interest in five- and six-coordinate Au(III) originally arose from findings that [Au(N-N)X_2]$^+$ species (N-N = 1,10-phenanthroline, 2,2′-bipyridyl, X = Cl or Br) undergo a redistribution in organic solvents with displacement of the chelated diamine [8]. It was suggested that Au(III) utilizes 6p6d orbitals in this reaction. The kinetics of these reactions have been the subject of a series of studies [9].

As to Au(2,2′-bpy)Cl_3, a polymeric structure built of planar [Au(2,2′-bpy)Cl_2]$^+$ cations bridged by chloride anions has been proposed on the basis of IR and Raman spectra [10]. The results of the X-ray analysis of Au(2,2′-bpy)$Cl_3 \cdot 2.25H_2O$ described in this paper reveal that this picture needs to be revised somewhat in that dinuclear species with a single chloro bridge between the two metal centres are present in the solid state.

We have prepared 'Au(2,2′-bpy)Cl_3' as a starting material for nucleobase complexes, specifically those of uracil. While reactions of Au(III) with DNA [11] and isolated nucleobases or models thereof [12] have been studied in several cases, to our knowledge no direct binding of Au(III) to uracil and thymine has been reported as yet. From the data available it appears that reactions of Au(III) with nucleobases are more complex than those of the isoelectronic Pt(II). For example, while $AuCl_3$(1-MeC) [12d] is formed from [$AuCl_4$]$^-$ and 1-methylcytosine, 1-MeC, [$AuBr_4$]$^-$ and cytosine interact with com-

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plete reduction of Au(III) to Au(I) and simultaneous bromination of cytosine at the 5-position [13]. 1-Methylhydantoine, although not a nucleobase but a heterocycle with close structural similarity to a pyrimidine nucleobase, reacts with $[AuCl_4]^-$ in alkaline medium with reduction to Au(I) and formation of a linear $[AuL_2]^-$ complex (L = deprotonated 1-methylhydantoine) [14]. Reactions of uridine with $[AuBr_4]^-$ [15] and of uracil with $[AuBr_4]^-$ and $[Au(CN)_2Br_2]^-$ [16] lead to Au(I) and 5-bromouracil and 5-bromo-6-hydroxy-5,6-dihydrouracil (uridine), yet not to metal coordination.

Experimental

Synthesis

$Au(2,2'\text{-}bpy)Cl_3 \cdot 2.25H_2O$ (**1**) was prepared in a way similar to that described by Block and Bailar [17] and Harris and Lockyer [8b]. Orange–yellow needles, isolated from aqueous solution and dried in air, displayed a somewhat variable water content, ranging from $1\text{–}2H_2O$ per Au. For example, Found: C, 24.5; H, 2.2; N, 5.7; Cl, 22.2; Au, 40.3. Calc. for 1.5-hydrate: C, 24.7; H, 2.3; N, 5.8; Cl, 21.9; Au, 40.5%. According to the results of the X-ray analysis, the water content actually is somewhat higher, at least 2.25 per Au, suggesting that water of crystallization is lost with time.

The bis(1-methyluracilato) complexes **2** were prepared as follows. **1** was dissolved in water and treated with 3 equiv. of $AgNO_3$, the precipitate filtered off and the resulting solution (0.2 M Au(III), pH 1.2) was reacted with 3 equiv. of 1-methyluracil, 1-MeUH, and 2 equiv. of NaOH at 50 °C. After 8 days, the reaction mixture was brought to dryness and unreacted components were extracted with 500 ml of MeOH. The undissolved, yellow residue was washed with MeOH, dried in air, and recrystallized from water (yield 49%). *Anal.* Calc. for $[Au(C_{10}H_8N_2)(C_5H_5N_2O_2)_2]NO_3 \cdot 7H_2O$ (**2a**): C, 30.35; H, 4.08; N, 12.38; O, 28.29; Au, 24.89. Found: C, 30.31; H, 3.98; N, 12.32; O, 28.22; Au, 24.8%. When $NaClO_4$ was added to an aqueous solution of **2a**, the corresponding perchlorate salt **2b** was obtained as yellow needles. Elemental analysis of **2b**, performed more than one year after sample preparation (sample stored at 22 °C), indicated that water of crystallization had been lost during this time: *Anal.* Calc. for $[Au(C_{10}H_8N_2)(C_5H_5N_2O_2)_2]ClO_4 \cdot 1.5H_2O$ (**2b'**): C, 32.91; H, 2.91; N, 11.52. Found: C, 32.9; H, 2.9; N, 11.5%.

Spectroscopy

IR spectra were recorded on Perkin-Elmer 577 and 783 spectrometers, ^1H NMR spectra on a Bruker AM 300. Reported chemical shifts (δ scale) are relative to sodium-3-(trimethylsilyl)propanesulfonate. Variations in pD (pH meter reading + 0.4) were achieved by addition of DNO_3 and NaOD, respectively.

X-ray Crystallography

Suitable crystals of **1** and **2b** were sealed under an atmosphere of argon into glass capillaries. Diffractometer measurements (Enraf-Nonius CAD 4) indicated triclinic unit cells and intensity data were collected in this setting. Reduced cell calculation (DELOS) [18] pointed to a monoclinic C-centered cell for **1** which was adopted for all further calculations. For **2b**, *P*1 was assumed as space group and confirmed by the successful refinement. Pertinent crystallographic data are summarized in Table 1. Intensity data were corrected for Lorentz–polarization effects and empirically for absorption. For the latter, scans at intervals of 10° around the diffraction vectors of 9 selected reflections near $\chi = 90°$ served to evaluate the transmissions. A non-linear correction for crystal decay (−15.1%) was applied for **1**. For **2b** (decay −1.6%), no correction was considered necessary.

The structures were solved by automated Patterson methods (SHELXS-86) [19] and completed by Fourier syntheses.

Refinement of 1

The hydrogen atoms at the aromatic ring system were calculated at idealized geometrical positions, those of the hydrate water molecules were neglected. The non-bridging Cl^- ion was found to be disordered and modelled as two half-occupied atoms. Their close proximity excluded the presence of two fully occupied water oxygen atoms at these positions. Further strong peaks in difference maps were interpreted as water molecules. Three of them could be refined anisotropically with full occupancy, three isotropically with half occupancy. Because there are two individual gold atoms in the unit cell, this amounts to the presence of 2.25 water molecules per individual gold cation. Again, close proximity of the latter to each other, and with respect to the partially occupied chloride atoms, further substantiated their treatment in split positions. The highest peaks in the final difference map strongly suggested the presence of further partially occupied water molecules. Refinement attempts failed, however. All other non-H atoms were refined anisotropically. The H atoms were kept constant with $U_{iso} = 0.05$ Å^2 (SHELX-76) [20].

Refinement of 2b

Four water molecules could be identified unambiguously in difference maps and their oxygen atoms were refined with anisotropic displacement parameters. All hydrogen atoms belonging to the gold cation were located and included in the struc-

TABLE 1. Crystal structure data for **1** and **2b**

	1	**2b**
Crystal dimensions (mm)	0.20 × 0.25 × 0.35	0.10 × 0.20 × 0.45
Formula	$C_{10}H_8AuCl_3N_2 \cdot 2.25H_2O$	$C_{20}H_{18}AuClN_6O_8 \cdot 4H_2O$
M_r	500.049	774.883
Crystal system	monoclinic	triclinic
Space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a (Å)	35.452(3)	7.930(1)
b (Å)	7.701(1)	12.606(1)
c (Å)	22.115(2)	13.768(1)
α (°)		93.46(1)
β (°)	90.67(1)	102.62(1)
γ (°)		96.74(1)
V (Å^3)	6037.3	1328.5
Z	16	2
D_{calc} (g/cm^3)	2.200	1.937
μ(Mo Kα) (cm^{-1})	102.5	56.9
F(000) (e)	3752	760
T (°C)	23	23
Radiation	Mo Kα	Mo Kα
λ (Å)	0.71069	0.71069
Monochromator	graphite	graphite
Scan	$\theta/2\theta$	$\theta/2\theta$
Scan width (°)	0.8 + 0.35 tan	1.0 + 0.35 tan ϑ
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.638	0.660
hkl range	±44, ±9, +28	+10, ±16, ±18
Standard reflections	$2\bar{4}0$, $\bar{1}\bar{8}\,0\bar{2}$, $\bar{8}0\,12$	$0\bar{6}\bar{1}$, $\bar{4}04$, $2\bar{1}6$
Reflections measured	21320	6404
Reflections unique	6544	6388
R_{int}	0.025	0.007
Reflections observed $F_o \geqslant 4\sigma(F_o)$	4603	5660
Relative transmission	0.71–1.00	0.68–1.00
Parameters refined	337	332
R^a	0.039	0.032
$R_w{}^b$	0.036	0.041
$(\text{Shift/error})_{max}$	0.52	0.84
$\Delta\rho_{fin}$ (max/min) (e/Å^3)	2.13/−1.43	+2.15/−1.33

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$, function minimized: $\Sigma w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$.

ture factor calculations as fixed atoms contributions (U_{iso} = 0.05 Å^2). Those of the water molecules were neglected. The ClO_4^- anion was found to be severely disordered with respect to its oxygen atoms. In the final refinement cycles it was treated as a regid idealized tetrahedron (Cl–O 1.50(1), O...O 2.45(1) Å; Cl anisotropic, O isotropic). All other non-H atoms were refined with anisotropic displacement parameters. The refinement was done using SHELX-76 [20]. The final difference map had the highest peaks around the disordered ClO_4^- atoms, and near the Au atom, but was featureless otherwise. Tables 2 and 3 contain the atomic coordinates for **1** and **2b**.

Results and Discussion

Crystal Structures

Figures 1 and 2 give two different views of $\{[(2,2'\text{-bpy})AuCl_2]_2\}Cl^+$ and Table 4 lists distances and angles about the two metal centers. The geometry of the bpy ligands is normal [21] (cf. 'Supplementary material') with virtually no tilting of the two halves of the ligands. The two N donors and the two terminal Cl ligands provide a square-planar coordination geometry about each Au, with normal bond lengths yet angles that deviate markedly from 90°, viz. 80.5(4)–95.8(3)°. The two Au atoms are connected via a common chloride bridge (Cl 3) through two long (≃3.2 Å) contacts. While these long contacts do not cause any measurable perturbation of the Au coordination plane towards a square pyramid, they are substantially shorter than expected for an essentially non-bonding interaction, which should be around 3.50 Å or longer. The shortest other contacts between Au and Cl are 3.594 Å (Au1...Cl1, 0.5 − x; 0.5 + y; 0.5 − z) and 3.417 Å (Au2...Cl41, 50% occupancy), thus supporting the description of **1** as a chloro bridged, dinuclear entity. As is evident

TABLE 2. Fractional atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms of **1**[a]

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Au1	0.2166(1)	0.1117(1)	0.3036(1)	0.036
Au2	0.1257(1)	−0.2708(1)	0.5101(1)	0.043
Cl1	0.2596(1)	−0.1012(4)	0.3183(1)	0.060
Cl2	0.1932(1)	−0.0451(4)	0.2254(1)	0.062
Cl11	0.1733(1)	−0.3363(4)	0.5750(2)	0.072
Cl12	0.1347(1)	−0.5318(4)	0.4650(2)	0.068
Cl3	0.1707(1)	−0.0199(4)	0.4192(1)	0.052
Cl41	0.0629(2)	−0.2716(9)	0.6260(3)	0.074
Cl42	0.0271(2)	−0.3698(9)	0.5624(3)	0.070
N1	0.1807(2)	0.3141(10)	0.2928(3)	0.034
N2	0.2378(2)	0.2689(10)	0.3691(3)	0.037
N11	0.0812(2)	−0.2009(12)	0.4584(4)	0.052
N12	0.1142(3)	−0.0382(11)	0.5476(4)	0.047
C1	0.1526(3)	0.3207(13)	0.2520(5)	0.046
C2	0.1310(3)	0.4694(18)	0.2470(6)	0.058
C3	0.1389(3)	0.6127(16)	0.2844(6)	0.054
C4	0.1675(3)	0.6018(13)	0.3239(5)	0.053
C5	0.1880(3)	0.4531(13)	0.3299(4)	0.036
C6	0.2194(3)	0.4260(13)	0.3734(4)	0.040
C7	0.2310(3)	0.5441(13)	0.4161(5)	0.054
C8	0.2593(4)	0.5051(16)	0.4555(5)	0.058
C9	0.2779(3)	0.3486(17)	0.4501(5)	0.060
C10	0.2659(3)	0.2317(13)	0.4073(5)	0.049
C11	0.0660(4)	−0.2930(17)	0.4127(6)	0.078
C12	0.0338(4)	−0.2373(20)	0.3813(6)	0.081
C13	0.0177(4)	−0.0819(20)	0.3973(6)	0.075
C14	0.0335(3)	0.0127(16)	0.4431(6)	0.056
C15	0.0651(3)	−0.0447(13)	0.4737(5)	0.044
C16	0.0834(3)	0.0436(13)	0.5225(5)	0.045
C17	0.0729(4)	0.2025(17)	0.5438(5)	0.060
C18	0.0932(5)	0.2805(18)	0.5891(6)	0.078
C19	0.1247(5)	0.1967(19)	0.6150(6)	0.079
C20	0.1340(4)	0.0360(16)	0.5918(5)	0.062
OH1	0.0547(3)	−0.1397(13)	0.2344(3)	0.043
OH2	0.1024(2)	0.0875(11)	0.3342(4)	0.083
OH3	0.0498(3)	0.3501(11)	0.3424(4)	0.091
OH4	0.0282(4)	−0.4696(20)	0.7318(6)	0.069
OH5	−0.0065(6)	−0.4133(25)	0.5580(9)	0.097
OH6	0.0499(6)	−0.2727(29)	0.6968(10)	0.123

[a] $U_{eq} = (U_1U_2U_3)^{1/3}$ with U_i being the eigenvalues of the U_{ij} matrix.

TABLE 3. Fractional atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms of **2b**[a]

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Au	0.1120(1)	0.2133(1)	0.3305(1)	0.026
O21	0.3206(5)	0.0583(4)	0.2518(4)	0.040
O41	−0.2476(6)	0.1103(4)	0.2116(4)	0.046
N11	0.1205(6)	−0.0491(4)	0.1322(4)	0.039
N31	0.0348(6)	0.0841(4)	0.2315(4)	0.031
C11	0.2591(10)	−0.1078(6)	0.1098(6)	0.049
C21	0.1691(8)	0.0326(5)	0.2072(5)	0.034
C41	−0.1403(8)	0.0578(5)	0.1846(5)	0.035
C51	−0.1803(9)	−0.0284(5)	0.1075(5)	0.042
C61	−0.0520(9)	−0.0775(5)	0.0851(5)	0.042
O22	−0.1826(5)	0.3478(4)	0.2991(3)	0.040
O42	0.2332(6)	0.2569(4)	0.1416(4)	0.056
N12	−0.1967(6)	0.3955(4)	0.1404(4)	0.041
N32	0.0265(6)	0.3033(4)	0.2192(4)	0.032
C12	−0.3533(10)	0.4480(6)	0.1413(6)	0.057
C22	−0.1234(8)	0.3485(5)	0.2241(5)	0.032
C42	0.1027(9)	0.3026(5)	0.1376(5)	0.040
C52	0.0180(10)	0.3534(6)	0.0542(5)	0.045
C62	−0.1265(11)	0.3967(6)	0.0593(5)	0.048
N1	0.2060(6)	0.3369(4)	0.4372(4)	0.033
N2	0.2049(6)	0.1291(4)	0.4468(4)	0.034
C1	0.1892(9)	0.4399(5)	0.4273(5)	0.041
C2	0.2671(9)	0.5176(5)	0.5033(6)	0.046
C3	0.3675(9)	0.4899(6)	0.5895(6)	0.047
C4	0.3860(9)	0.3838(6)	0.5991(5)	0.044
C5	0.3010(8)	0.3067(5)	0.5227(5)	0.035
C6	0.2995(8)	0.1904(5)	0.5288(5)	0.034
C7	0.3800(9)	0.1434(6)	0.6113(5)	0.045
C8	0.3608(10)	0.0339(6)	0.6097(6)	0.046
C9	0.2626(10)	−0.0290(6)	0.5261(6)	0.046
C10	0.1841(9)	0.0209(5)	0.4451(5)	0.040
Cl	−0.0348(3)	0.2807(2)	0.6974(2)	0.066
O1	−0.2178(4)	0.2297(2)	0.6951(2)	0.154
O2	−0.0242(3)	0.3039(2)	0.5928(2)	0.255
O3	0.0905(3)	0.2054(2)	0.7355(2)	0.229
O4	0.0036(3)	0.3835(2)	0.7632(2)	0.319
OH1	0.4891(6)	0.1772(4)	0.0623(4)	0.055
OH2	−0.4600(6)	0.2377(4)	0.3691(4)	0.058
OH3	0.6743(9)	0.4335(6)	−0.1768(5)	0.092
OH4	0.4405(9)	0.2804(6)	−0.1185(6)	0.100

[a] U_{eq} defined as in Table 2.

from Fig. 2, the two (2,2′-bpy)$AuCl_2^+$ units are virtually parallel with a minimum distance of 6.18 Å and a maximum distance of 6.34 Å. A view along the Au1–Au2 vectore (not shown) reveals that the bpy ligands adopt a nearly eclipsed arrangement (torsional angle *c*. 35°) and furthermore, that the bridging chloride Cl3 is directed *toward* the two bpy ligands. The Au1–Cl3–Au2 angle is 160.9(3)°. In a sense, the bridging chloride can be considered almost on the verge of being sandwiched between the two bpy ligands. While displacement of Cl3 toward the opposite direction in principle might lead to a shorter contact of the parallel bpy ligands, steric clash with the terminal chlorides (in particular Cl1, Cl2, and Cl12) apparently prevents this alternative.

Figure 3 depicts the $[(2,2'\text{-bpy})Au(1\text{-MeU})_2]^+$ cation of **2b**. Table 5 gives selected distances and angles of this compound. Au is surrounded by two nitrogens (N1, N2) from the bpy ligand and two nitrogens (N31, N32) of the 1-MeU ligands, leading to a square-planar coordination geometry about the heavy metal. Exocyclic oxygens of the two 1-MeU ligands are almost equally distant from Au (O21, 3.002 Å; O41, 3.055 Å; O22, 3.016 Å; O42, 3.023 Å) thus ruling against any extension of the Au co-

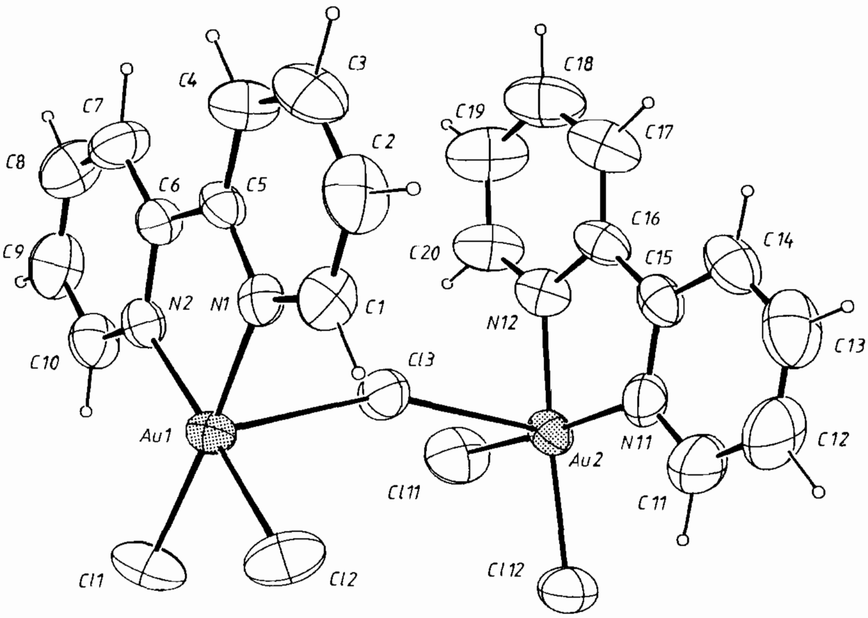

Fig. 1. ORTEP drawing of dinuclear $[(2,2'\text{-bpy})Cl_2AuClAuCl_2(2,2'\text{-bpy})]^+$ entity of **1**.

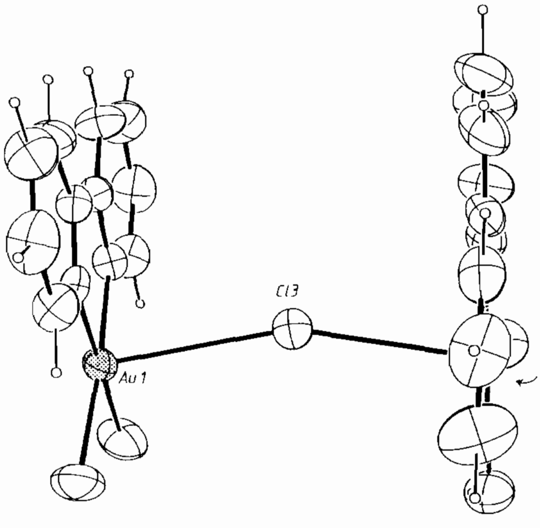

Fig. 2. View of dinuclear entity of **1** demonstrating the almost parallel arrangement of the two 2,2′-bpy ligands.

TABLE 4. Selected interatomic distances (Å) and angles (°) about the Au atoms in 1

Au1–Cl1	2.260(3)	Au1–Cl2	2.259(3)
Au1–N1	2.025(8)	Au1–N2	2.026(8)
Au2–Cl11	2.259(3)	Au2–Cl12	2.268(3)
Au2–N11	2.014(9)	Au2–N12	2.018(9)
Au1–Cl3	3.212(3)	Au2–Cl3	3.223(3)
Cl1–Au1–Cl2	87.9(1)	Cl1–Au1–N1	176.1(2)
Cl2–Au1–N1	95.5(2)	Cl1–Au1–N2	95.0(2)
Cl2–Au1–N2	175.4(2)	N1–Au1–N2	81.4(3)
Cl2–Au1–Cl3	90.2(1)	Cl2–Au1–Cl3	104.8(1)
Cl3–Au1–N1	90.7(2)	Cl3–Au1–N2	78.8(1)
Cl11–Au2–Cl12	88.5(1)	Cl11–Au2–N11	174.9(3)
Cl12–Au2–N11	95.8(3)	Cl11–Au2–N12	95.2(3)
Cl12–Au2–N12	176.1(3)	N11–Au2–N12	80.5(4)
Cl11–Au2–Cl3	99.2(1)	Cl12–Au2–Cl3	100.6(1)
Cl3–Au2–N11	82.9(4)	Cl3–Au2–N12	80.1(4)
Au1–Cl3–Au2	160.9(3)		

ordination sphere beyond four. These oxygen atoms are situated such that they rather shield the axial positions of the four-coordinated planar gold atom. Although the oxygen of a water molecule (OH 2) has a moderately short distance of 3.293 Å from Au, it exceeds that of the sum of the van der Waals radii. It is also much longer than the 2.77 Å found in *cis*-dichloro(dihydroxy-di-2-pyridylmethane)gold(III) chloride [22]. Since this water molecule appears to be H-bonded to O21 of one of the two 1-MeU ligands (Table 6), its location seems to be dictated primarily by this hydrogen bond and less so by any significant O...Au interaction. Consequently, there is no measurable perturbation of the AuN_4 plane that might justify description of **2b** as a pentacoordinated Au species.

The two 1-MeU ligands in 2b are arranged head-to-tail, as are the 1-MeU ligands in *cis*-$(NH_3)_2Pt(1\text{-MeU})_2 \cdot 4H_2O$ [23], the only other bis(uracil) metal complex characterized by X-ray analysis to date. Dihedral angles between 1-MeU and metal coordination planes are also very similar in both compounds, 112° and 114° in **2b** and 112° and 119° in the Pt complex.

Geometries of both the bpy and the 1-MeU ligands are normal. CO distances within the two 1-MeU ligands (C2–O2, 1.220(7) and 1.225(7) Å;

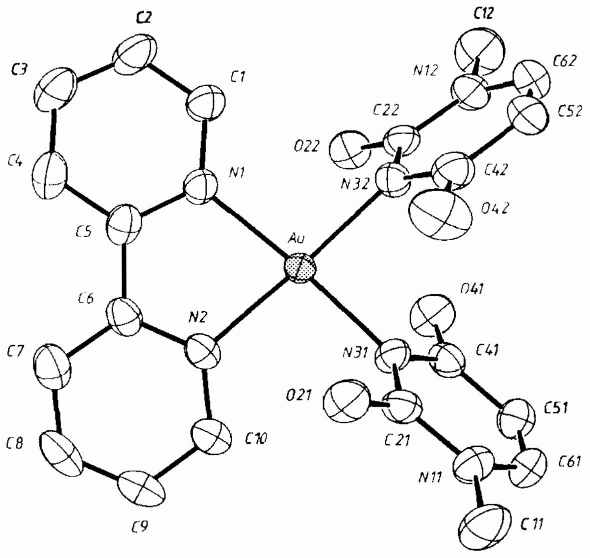

Fig. 3. Cation $[(2,2'\text{-bpy})\mathrm{Au}(1\text{-MeU})_2]^+$ of 2b with atom numbering scheme.

C4–O4, 1.234(8) and 1.241(7) Å) display no significant differences and furthermore are not significantly longer than in free 1-MeUH (C2–O2, 1.226(1) Å; C4–O4, 1.241(2) Å) [24]. There is, however, a clear trend of the internal uracil angle at N3 (C2–N3–C4) in **2b** toward larger values (124.3(5)°, 124.9(5)°) as compared to related Pt–uracil (thymine) entities, e.g. 120.7(5)° and 120.8(5)° in *cis*-$[(\mathrm{NH_3})_2\mathrm{Pt}(1\text{-MeU})_2\mathrm{Pd(en)}]^{2+}$ [25] or 120.7(9)° in *cis*-$(\mathrm{NH_3})_2\mathrm{Pt}(1\text{-MeT})\mathrm{Cl}$ [26]. The effect of the Au(III) electrophile on this angle thus is closer to that of a proton (cf. 126.6(1)° in 1-MeUH [24]) than of a Pt(II) electrophile.

TABLE 5. Selected interatomic distances (Å) and angles (°) in 2b

Metal coordination sphere			
Au–N31	2.004(5)	Au–N32	2.008(5)
Au–N1	2.028(5)	Au–N2	2.027(5)
N31–Au–N32	87.9(2)	N31–Au–N1	175.1(2)
N32–Au–N1	96.4(2)	N31–Au–N2	94.8(2)
N32–Au–N2	177.2(2)	N1–Au–N2	80.9(2)
1-MeU ligands			
O21–C21	1.220(7)	O41–C41	1.241(7)
N11–C11	1.470(8)	N11–C21	1.371(8)
N11–C61	1.374(8)	N31–C21	1.400(7)
N31–C41	1.389(7)	C41–C51	1.429(9)
C51–C61	1.333(9)	O22–C22	1.225(7)
O42–C42	1.234(8)	N12–C12	1.476(8)
N12–C22	1.374(8)	N12–C62	1.353(9)
N32–C22	1.390(7)	N32–C42	1.388(8)
C42–C52	1.425(9)	C52–C62	1.34(1)
C11–N11–C21	117.0(5)	C11–N11–C61	122.4(6)
C21–N11–C61	120.6(5)	Au–N31–C21	115.4(4)
Au–N31–C41	120.0(4)	C21–N31–C41	124.3(5)
O21–C21–N11	122.1(6)	O21–C21–N31	121.5(6)
N11–C21–N31	116.4(5)	O41–C41–N31	118.5(6)
O41–C41–C51	125.6(6)	N31–C41–C51	115.9(6)
C41–C51–C61	119.5(6)	N11–C61–C51	123.3(6)
C12–N12–C22	118.5(6)	C12–N12–C62	119.9(6)
C22–N12–C62	121.6(6)	Au–N32–C22	115.8(4)
Au–N32–C42	118.6(4)	C22–N32–C42	124.9(5)
O22–C22–N12	122.9(6)	O22–C22–N32	121.6(6)
N12–C22–N32	115.4(6)	O42–C42–N32	118.5(6)
O42–C42–C52	125.7(7)	N32–C42–C52	115.8(6)
C42–C52–C62	119.1(6)	N12–C62–C52	123.2(7)

TABLE 6. Hydrogen bonding interaction (Å) in 2b[a]

O21...OH2	(1 + x, y, z)	2.86
O22...OH2	(x, y, z)	2.84
O41...OH1	(x – 1, y, z)	2.84
O41...OH1	(x, y, z)	2.76
OH1...OH4	(x, y, z)	2.85
OH3...OH4	(x, y, z)	2.79

[a] Between water molecules and between water molecules and exacyclic 1-MeU oxygens. Additional short contacts between water and $\mathrm{ClO_4}^-$ are not listed.

Comparison with Pt(II) and Pd(II) Analogues

Comparison of **2** with the isoelectronic $\mathrm{Pt}(2,2'\text{-bpy})(1\text{-MeU})_2$ complex **3** [25] and the Pd analogue **4** [27] reveals several noteworthy differences, referring both to spectroscopic and reactivity aspects. In the IR spectra, the most evident difference exists in the double bond stretching region. While **3** and **4** display an intense band at 1570 $\mathrm{cm^{-1}}$, no such band is seen with **2**. This band has previously been found characteristic of Pt(II) or Pd(II) coordination to N3 of 1-MeU, 1-methylthymine, uracil or thymine [28] and assigned to a $\mathrm{O2\overset{..}{-}C2\overset{..}{-}N3\overset{..}{-}C4\overset{..}{-}O4}$ stretching mode, indicative of a marked decrease in C(4)O(4) double bond character and a concomitant delocalization of negative charge into the heterocyclic ring. Rather, the appearance of **2** in this spectral region (broad band at 1640 $\mathrm{cm^{-1}}$) is remarkably similar to that of free 1-MeUH (1660vs $\mathrm{cm^{-1}}$; 1695sh $\mathrm{cm^{-1}}$). The tentative conclusion that the delocalization of the –1 charge of the 1-MeU ligand in **2** is considerably smaller than in **3**, **4** or related Pt(II) and Pd(II) complexes gets additional support from the apparent low basicity of 1-MeU in **2** and the low affinity for other metal electrophiles (*vide infra*). Complexes of type *cis*-$\mathrm{a_2PtL_2}$ (a = amine, L = 1-MeU or 1-MeT) undergo protonation below pH $\simeq$ 4 (p$K_{\mathrm{a1}} \simeq 2$ [29]) and consequently show strongly pH dependent chemical shifts in acidic medium. In contrast, the 1-MeU resonances of **2** are independent of pH in the pH range 12–0 with chemical shifts for H5 and H6 (yet not $\mathrm{N\text{-}CH_3}$) virtually identical with those of free 1-MeUH (Table 7). Low $\mathrm{H^+}$ affinity of the Au(1-MeU) entity is paralleled by the apparent non-reactivity of **2** towards heterometals such as $\mathrm{Ag^+}$

TABLE 7. ^{1}H NMR chemical shifts[a]

	H6	H5	CH_3	bpy	pD
1-MeUH	7.60d	5.78d	3.36s		0–8
1-MeU	7.45d	5.71d	3.31s		11
2	7.61d	5.79d	3.42s	8.71; 8.66; 7.97m	0
	7.61d	5.79d; 5.80d	3.41s	8.71; 8.65; 7.95	1.8
	7.61d	5.79d, 5.80d	3.41s	8.71; 8.65; 7.95	7.4
	7.61d	5.78d, 5.79d	3.41s	8.81; 8.64; 7.95	11.3
3	7.47d	5.69d	3.35s	8.41; 8.30; 7.75m	7.7
	7.50d	5.687d; *c.* 5.684d	3.38s	8.44; 8.33; 7.58m	2.9
4	7.45d	5.590d; 5.587d	3.34s	8.43; 8.30; 8.10; 7.60m	
5	7.71d	5.94d	3.49s	9.02; 8.57; 8.10; 7.92	0
5′	7.70d	5.94d	3.49s	9.00; 8.55; 8.14; 7.92	12.3

[a] In ppm (δ scale); solvent D_2O except **4** ($D_2O:(CD_3)_2CO$ = 1:1); d = doublet; $^3J \simeq 7.5$ Hz; s = singlet; m = multiplet.

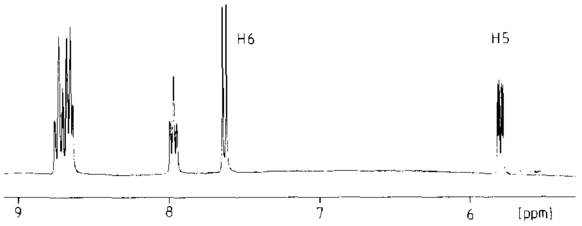

Fig. 4. Lowfield section of 300 MHz ^{1}H NMR spectrum of **2b** in D_2O (pD 1.8) with H5 resonances of 1-MeU ligands doubled due to presence of two rotamers.

or Cu^{2+}. Again, this situation contrasts findings that the neutral, isoelectronic Pt(II) species **3**, as related Pt(II) and Pd(II) complexes, readily form heteronuclear complexes [23, 25, 30].

A noteworthy detail of the ^{1}H NMR spectrum of **2** refers to the doubling of the H5 doublet of the 1-MeU ligand (Δδ 3.1 Hz). In neutral and moderately acidic medium (pD $\geqslant$ 1), the relative intensities of both doublets are 1:1 (Fig. 4), whereas in strongly alkaline medium (pD 12), the upfield doublet is somewhat more intense. Only a pD 0 does H5 consist of a single doublet. Neither H6 nor N-CH_3 show any signs of doubling. A similar situation applies to the isoelectronic Pt(II) complex **3** (Δδ ≃ 1.6 Hz) and the Pd(II) analogue **4** (Δδ = 1 Hz) with the two sets of H5 resonances resolved at high resolution only, however. In related complexes of 1-MeT, e.g. (2,2′-bpy)Pt(1-MeT)$_2$, both C(5)CH_3 and N(1)-CH_3 resonances are doubled, yet not H6 [27]. Since this phenomenon is not Au specific, it most likely is due to the presence of two rotamers (head–head and head–tail) in solution. With *cis*-$(NH_3)_2$Pt(1-MeU)$_2$ the rotation of the head–tail rotamer (C_2 local symmetry) into the head–head rotamer (C_s local symmetry) has been deduced on the basis of crystal structures of the bis(1-MeU) complex and di- and trinuclear derivatives [23, 30, 31].

Finally, we note that the 2,2′-bpy resonances in the Au(III) complex **2** and the analogous Pt(II) (**3**) and Pd(II) complex (**4**) display distinct differences which, at least for Pt(II) and Pd(II), are relatively insensitive of the bound nucleobase (1-MeU and 1-MeT). In **4**, four sets of aromatic protons are clearly discernible, centered at 7.60, 8.10, 8.30 and 8.43 ppm, whereas both with **3** and with **2** only the β proton [32] (**3**, 7.58 ppm; **2**, 7.95 ppm) is well separated, whereas γ and δ protons overlap (**3**, 8.33 ppm; **2**, 8.65 ppm) and are close to the postion of the α proton at *c.* 8.71 (**2**) and 8.44 ppm (**3**).

Decomposition Reactions of 2

^{1}H NMR spectra of **2** are indicative of a slow decomposition of **2** in strongly acidic medium. At pD ≃ 0 (DNO_3), within three days at 22 °C, *c.* 60% of **2** has reacted according to

$$\underset{\mathbf{2}}{[(\mathrm{bpy})\mathrm{Au}(1\text{-MeU})_2]^+} + \mathrm{D}^+ \xrightarrow{\mathrm{D_2O}} \underset{\mathbf{5}}{[(\mathrm{bpy})\mathrm{Au}(1\text{-MeU})(\mathrm{D_2O})]^{2+}} + 1\text{-MeUD}$$

as judged from the appearance of two new signal sets in 1:1 ratio. 1-MeU resonances of the new 1:1 complex occur downfield from those of **2** (Table 7). The rather slow decomposition probably reflects the poor basicity of the 1-MeU ligand which impedes formation of a [(bpy)Au(1-MeU)(1-MeUD)]$^{2+}$ precursor.

In strongly alkaline solution, decompostion of **2**, presumably via a nucleophilic attack of OH^- on Au, is more rapid. Within *c.* 1 h at 22 °C, two thirds of **2** are converted into free 1-MeU and [(bpy)Au(1-MeU)OH]$^+$, with some additional decomposition to (bpy)Au(OH)$_2$ taking place as well (peaks due to free 1-MeU slightly more intense than those of the Au complex formed)

$$\underset{2}{[(bpy)Au(1\text{-}MeU)_2]^+} + OD^- \longrightarrow \underset{5'}{[(bpy)Au(1\text{-}MeU)OD]^+} + 1\text{-}MeU$$

$$[(bpy)Au(1\text{-}MeU)OD]^+ + OD^- \longrightarrow [(bpy)Au(OD)_2]^+ + 1\text{-}MeU$$

The close similarity of chemical shifts of both the 1-MeU and bpy ligands in 5 and 5′ are consistent with their proposed structures and rule against any head–tail dimerization of 5

$$2[(bpy)Au(1\text{-}MeU)(D_2O)]^{2+} \not\longrightarrow 2D_2O + [(bpy)Au(1\text{-}MeU)_2Au(bpy)]^{4+}$$

This reaction is expected to be unfavorable on the basis of the above mentioned weak basicity of exocyclic oxygens in a Au(1-MeU) entity and in addition due the high positive charge of the dinuclear species. Thus, Au(III) also behaves differently in this respect from related $[A_2Pt(L)H_2O]^+$ species (L = 1-MeU or 1-MeT) which readily dimerize [33].

Supplementary Material

Additional structural details and lists of observed and calculated structure factors are available on request from the Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen under code CSD-53715.

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