1-Methyluracil (Hmeu) as a Tetradentate Ligand: Crystal Structure of *trans*-$(NH_3)_2Pt(meu)_2Ag_2(NO_3)_2(H_2O){\cdot}H_2O$

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In the heteronuclear complex *trans*-$(NH_3)_2Pt(C_5H_5N_2O_2)_2Ag_2(NO_3)_2(H_2O){\cdot}H_2O$ trinuclear Pt,Ag_2,L_2 (L = 1-methyluracil anion, meu) units, containing Pt co-ordinated to N(3) of meu and Ag atoms bound through mixed O(4), O(2) co-ordination, are linked through additional binding between O(4) of meu and Ag of the adjacent molecule, thus creating a polymeric arrangement of Pt,Ag_2,L_2 with tetradentate meu and bridging O(4) oxygens.

The model nucleotides 1-methyluracil (Hmeu) and 1-methylthymine (Hmet) exhibit, when bound to Pt^{II} through the N(3) site, a remarkable tendency to use their exocyclic oxygens for additional metal co-ordination. As a consequence, a variety of dinuclear Pt^{II} and heteronuclear $Pt_xM_yL_z$ complexes have been isolated and characterized.[1] Though the biological relevance of this finding with respect to the antitumour activity of Pt co-ordination compounds[2] is uncertain, the observed metal binding patterns are of general significance to metal ion–nucleic acid interactions and of particular interest for the elucidation of the structure of the so called 'platinum pyrimidine blues,' a class of potent antitumour agents formed on the reaction of *cis*-$(NH_3)_2Pt(H_2O)_2^{2+}$ with uracil, thymine, and related ligands.[3] This report of the crystal structure of bis-μ-(1-methyluracilato)-*trans*-diammineplatinum(II)dinitrato aquadisilver monohydrate, *trans*-$(NH_3)_2Pt(C_5H_5N_2O_2)_2Ag_2(NO_3)_2(H_2O){\cdot}H_2O$, represents the first example of tetradentate uracil and demonstrates that the basicity of the O(4) oxygen is sufficient to accommodate binding of two metals simultaneously.

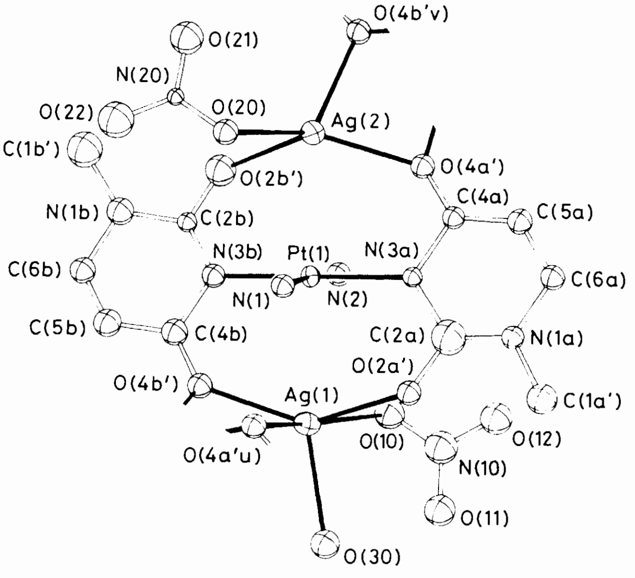

Figure 1. Segment of *trans*-$(NH_3)_2Pt(meu)_2Ag_2(NO_3)_2(H_2O)$ within the polymeric chain. For clarity, the bridging O(4) oxygens of the adjacent molecules related by the symmetry transformations u and v are also included. The shortest intermolecular Ag–Ag interactions are: *d*[Ag(1)–Ag(2u)] = *d*[Ag(2)–Ag(1v)] = 3.597 Å. The non-co-ordinating water molecule O(31) within the crystal lattice is omitted. It forms hydrogen bonds with the oxygens of one of the NO_3^- ions [O(20) and O(22)].

The complex was prepared by dissolving the almost water-insoluble *trans*-$(NH_3)_2Pt(meu)_2$ (100 mg)† in an aqueous solution of $AgNO_3$ (200 mg in 20 ml of H_2O), filtering off any undissolved material, and allowing the colourless solution to evaporate at 3 °C. Recrystallization from 3 ml of H_2O gave colourless crystals (yield 180 mg).‡ A segment of the polymeric arrangement of the trinuclear Pt,Ag_2,L_2 molecules is shown in Figure 1.§ Pt binding occurs through N(3) of the two meu rings which are arranged head-to-tail. While this arrangement may not be considered unusual and is, for example, also observed in *cis*-$(NH_3)_2Pt(meu)_2$,[1a] the compound described here is the first example of a heteronuclear complex derived from $(NH_3)_2PtL_2$ (L = meu or met) having this geometry. In all previously studied cases the two nucleotides are arranged head-to-head with the heterometal atoms co-ordinating successively at O(4), O(4) and only then at O(2), O(2).

The co-ordination geometry of Pt is square-planar. Pt–NH_3 [2.028(23), 2.131(21) Å][4] and Pt–N(meu) distances [1.983(24), 2.084(21) Å][1a] are normal and the angles around Pt are close to 90°. Pt is roughly coplanar with one of the meu ligands (ring a), but considerably (0.28 Å) out of the plane of the other (ring b). Pt is separated from the two Ag atoms by 2.896(3) [Ag(1)] and 2.863(3) Å [Ag(2)], similar to the Pt–Ag distances in *cis*-$[(NH_3)_2Pt(meu)Ag]_2(NO_3)_4$,[1d] and *cis*-$[(NH_3)_4Pt_2(met)_4Ag]NO_3$.[1e] The three heavy metals are not exactly colinear but form a 169.7(1)° angle around Pt.

Ag(2) exhibits a severely distorted tetrahedral co-ordination geometry, with bonding distances of 2.313(20) Å to O(4a'), 2.447(26) Å to O(2b'), 2.411(21) Å to O(20) of the co-ordinated NO_3^-, and 2.368(21) Å to O(4b'v) of the adjacent molecule with symmetry transformation v = $x - 1/2$, $-y + 1/2$, z. Angles around Ag(2) range from 79.3° [O(4a')–

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† *trans*-$(NH_3)_2Pt(meu)_2$ was obtained from *trans*-$[(NH_3)_2Pt(H_2O)_2](NO_3)_2$ and 2—3 equiv. of meu in a similar way to the *cis*-isomer.[1a] Satisfactory elemental analyses were obtained for C, H, N, and Pt.

‡ Satisfactory elemental analyses were obtained for C, H, N, and Ag.

§ *Crystal data:* $C_{10}H_{20}Ag_2N_8O_{12}Pt$, $M = 855.21$, orthorhombic, space group $Pna2_1$, $a = 13.206(6)$, $b = 7.238(9)$, $c = 22.051(10)$ Å, $U = 2107.7$ Å^3, $Z = 4$, $D_m = 2.68$, $D_c = 2.695$ g cm^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å. Data were collected on a Philips PW 1100 diffractometer using a θ/2θ technique ($\theta_{max.}$ 23°) for a crystal of dimensions 0.2 × 0.2 × 0.2 mm. Lorentz, polarisation, and empirical absorption corrections were applied. 1744 Reflections were collected and 1469 reflections with $F_o > 2\sigma(F_o)$ were used for the calculations. Pt and Ag atoms were refined anisotropically, the other atoms isotropically. The structure was refined to $R = 0.058$, $R_w = 0.063$ with $w = 1.635/[\sigma^2(F) + 0.0018 F^2]$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

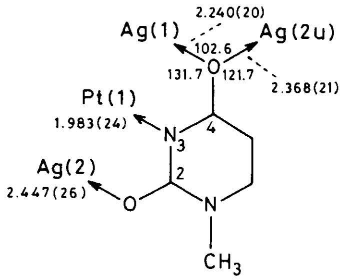

Figure 2. Schematic picture of the tetradentate nature of meu in the title compound. Bond distances (Å) and angles around O(4) (°) refer to ring b.

Ag(2)-O(4b'v)] to 141.0° [O(20)-Ag(2)-O(4a')]. The co-ordination sphere of Ag(1) is, to a first approximation, that of a trigonal bipyramid. Ag(1) forms three strong bonds with the equatorial donor atoms O(4b') [2.240(20) Å], O(2a') [2.327(20) Å], and the co-ordinated aqua ligand O(30) [2.418(24) Å], and in addition has two long contacts to the axial donors O(10) of the second NO_3^- [2.810(26) Å] and O(4a'u) [2.838(22) Å] of the neighbour at the other end of the molecule, related by the symmetry transformation u = x + 1/2, $-y$ + 1/2, z.

Certainly the most interesting aspect of this structure is the role of the exocyclic oxygens O(4a') and O(4b') of the two meu rings in linking the Ag atoms of adjacent molecules, thus creating an infinite array of Pt,Ag_2,L_2 units. While the intermolecular interaction between Ag and O(4) of ring a is rather weak [2.838(22) Å], it is strong in the case of ring b, giving rise to an intermolecular Ag–O distance that is shorter [2.368(21) Å] than some of the intramolecular Ag–O separations.

The metal bridging function of O(4) of meu is responsible for the fact that there are four simultaneously bound metal atoms in the compound, through N(3), O(2), and twofold through O(4), Figure 2. Previously a maximum of three metal atoms bound to a meu[1b,1d] or a met[5] ligand has been observed. The property of O(4) to act as a bridge between two metal atoms provides additional evidence for the increased basicity of this site as a consequence of Pt substituting the proton at N(3) of the neutral ligand, a conclusion deduced from pK measurements,[6] vibrational spectroscopy,[1e,5c] and the affinity for additional metals.[1,5]

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