

(type I in Fig. 1) stabilized by a water bridge shows the importance of such a water molecule in keeping the structure in the specific configuration. Consequently, though the present analysis has failed to present the *anti* structure (type II in Fig. 1), its possibility cannot be ruled out in different hydration environments around Ag–polyinosinic acid polymers. Furthermore, nucleic acid structures are themselves constrained and their sugar–phosphate backbones are additional factors affecting structures of nucleic acids by interacting with water molecules and/or various ions.

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## Structure of (1-Methyluracilato)silver(I), [Ag(C<sub>5</sub>H<sub>3</sub>N<sub>2</sub>O<sub>2</sub>)]

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**Abstract.**  $M_r = 233.0$ , monoclinic,  $C2/c$ ,  $a = 12.537$  (9),  $b = 10.278$  (8),  $c = 9.918$  (6) Å,  $\beta = 104.84$  (5)°,  $V = 1223$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 2.53$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71068$  Å,  $\mu(\text{Mo } K\alpha) = 3.48$  mm<sup>-1</sup>,  $F(000) = 896$ , room temperature,  $R = 0.099$  for 479 observed reflections. The complex is a one-dimensional polymer in which one of the two independent Ag<sup>+</sup> ions is linearly bonded to the two 1-methyluracilate ligands through the deprotonated N(3) sites and another Ag<sup>+</sup> ion tetrahedrally to the four ligands through the two O(2) and two O(4) sites; an N(3)–metal–bonded base–base pair, which involves an inversion center at the metal site, is arranged in *anti* configuration with respect to the N–Ag–N bond and is further cross-linked by two additional metal ions with the formation of eight-membered chelate rings,  $\overline{\text{Ag}(\text{I})\text{—N}(3)\text{—C}(2)\text{—O}(2)\text{—Ag}(2^{\text{I})}\text{—O}(4^{\text{I})}\text{—C}(4^{\text{I})}\text{—N}(3^{\text{I}})}$ .

**Introduction.** Recently, Shin & Eichhorn (1980) have reported that Ag<sup>+</sup> ions react with polyuridylic acid to form

a 1:1 complex at low pH, with one proton released, and they have proposed a double-helical structure with N(3)–Ag–O bonding. In order to aid in the prediction of the structure that might be expected for the Ag–polyuridylic acid system, we have determined the crystal structure of the 1:1 Ag–1-methyluracilate complex. The analogous complex (1-methyl-thyminato)Ag<sup>I</sup> has been reported (Guay & Beauchamp, 1979).

**Experimental.** Colourless needles, elongated along *c*, slightly photosensitive, obtained from an aqueous solution (pH *ca* 5) containing 1-methyluracil and AgNO<sub>3</sub> (10<sup>-4</sup> mol, 1:1 ratio). Crystal 0.02 × 0.03 × 0.15 mm. Rigaku automated four-circle diffractometer, graphite-monochromated Mo *K*α radiation. Cell parameters refined by least squares with 13 independent  $2\theta$  values.  $2\theta \leq 45^\circ$  ( $\pm h \pm k + l$  set),  $\omega$ – $2\theta$  scan mode. 956 reflections measured, 479 with  $F_o > 3\sigma(F_o)$  used for the structure determination. Three reference

reflections: no systematic intensity variation. No absorption correction because of the small crystal size. Structure solved by Patterson and Fourier methods. Block-diagonal least-squares refinement with anisotropic thermal parameters for the two Ag atoms and isotropic ones for the other atoms (H atoms not located);  $\sum w(F_o - |F_c|)^2$  minimized,  $w = 1/\sigma(F_o)^2$ ; final  $R = 0.099$  and  $R_w = 0.097$  for 479 observed reflections. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).  $(\Delta/\sigma)_{\max} = 0.26$ . Max. peak in final  $\Delta\rho$  map  $2.0 \text{ e } \text{Å}^{-3}$  near Ag atom. Calculations carried out on a FACOM M380 computer at the Institute of Physical and Chemical Research with the UNICSIII program system (Sakurai & Kobayashi, 1979).

Table 1. *Positional parameters* ( $\times 10^4$  for Ag atoms,  $\times 10^3$  for others), *equivalent isotropic temperature factors for Ag atoms* ( $B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$ ) and *isotropic ones for others, with e.s.d.'s in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
Ag(1)	0	0	0	3.0 (0.1)
Ag(2)	0	1472 (5)	2500	3.9 (0.1)
C(1)	237 (3)	222 (4)	-334 (4)	4.3 (0.8)
N(1)	176 (2)	242 (3)	-218 (3)	3.3 (0.6)
C(2)	133 (2)	143 (3)	-169 (3)	2.5 (0.6)
O(2)	145 (2)	28 (2)	-208 (2)	3.5 (0.5)
N(3)	80 (2)	158 (3)	-63 (2)	2.3 (0.5)
C(4)	65 (3)	282 (4)	-12 (3)	3.3 (0.7)
O(4)	21 (2)	297 (3)	71 (3)	4.9 (0.6)
C(5)	110 (3)	392 (4)	-70 (4)	4.2 (0.8)
C(6)	164 (3)	370 (4)	-179 (4)	3.8 (0.7)

**Discussion.** Final atomic parameters are in Table 1.\* A perspective view of the complex is drawn in Fig. 1 with bond lengths and angles. The 1-methyluracilate ligand coordinates to three Ag atoms through the deprotonated ring nitrogen N(3) and the exocyclic carbonyl O atoms O(2) and O(4). There exist two different Ag atoms. Ag(1), which occupies a crystallographic inversion center, must be exactly linearly bonded to two ligand N(3) atoms, forming a metal-bridged base-base pair  $\text{Ag}(\mu)_2$  which is arranged in *anti* configuration with respect to the N—Ag—N bond. Ag(1) is out of the base plane by  $0.19 (5) \text{ Å}$  and, consequently, the two symmetry-related parallel bases in  $\text{Ag}(\mu)_2$  deviate from each base plane by an average distance of  $0.37 (2) \text{ Å}$ . On the other hand, Ag(2), lying on a crystallographic twofold axis along *b*, is tetrahedrally bonded to two symmetry-related  $\text{Ag}(\mu)_2$  units through two O(2) and two O(4) atoms. Thus each  $\text{Ag}(\mu)_2$  unit is connected by each Ag(2) atom, thereby yielding a one-dimensional polymer of the complex with a zigzag array of Ag atoms along *c*,  $[\dots\text{Ag}(2)\dots\text{Ag}(1)\dots\text{Ag}(2)\dots]_n$  [ $\text{Ag}(1)\dots\text{Ag}(2) = 2.883 (3) \text{ Å}$ ,  $\text{Ag}(2)\dots\text{Ag}(1)\dots\text{Ag}(2) = 180.0^\circ$ ,  $\text{Ag}(1)\dots\text{Ag}(2)\dots\text{Ag}(1) = 116.7 (2)^\circ$ ] (Fig. 2). Within the polymer chain, both bases bridged by Ag(2) *via* Ag—O(2) bonds overlap around a twofold axis along *b* with an average distance of  $3.4 (2) \text{ Å}$ . This O(2)—metal-bridged base-base stacking is also observed in [Ag(1-methylcytosine) ( $\text{NO}_3$ )] ( $3.34 \text{ Å}$  spacing) (Kistenmacher, Rossi & Marzilli, 1979). It should be noted that a large deviation of the metal-ion position from the base plane,  $1.28 (6) \text{ Å}$  in the present complex and  $1.44$  and  $1.90 \text{ Å}$  in Ag(1-methylcytosine), clearly shows the ability of O(2) to form out-of-plane coordination. This is also the

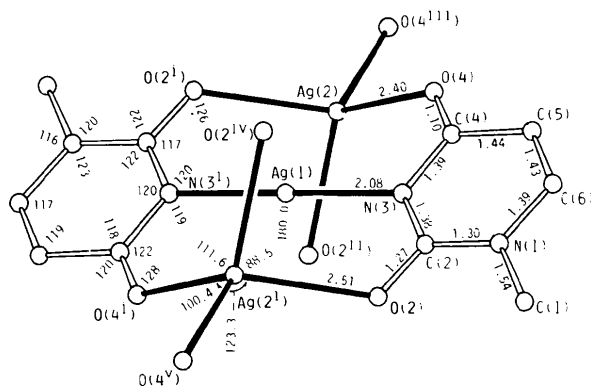


Fig. 1. A perspective view of the basic dimeric unit in (1-methyluracilato)Ag with bond lengths (Å) and angles ( $^\circ$ ), showing the *anti* configuration of the unit with respect to the N—Ag—N bond and also showing the formation of the eight-membered chelate rings. Covalent and coordinative bonds are respectively drawn as open and solid (also in Fig. 2). The e.s.d.'s are as follows: Ag—N(or O)  $0.03$ , C—C(or N or O)  $0.05 \text{ Å}$ ; O—Ag—O  $0.09^\circ$ , Ag—N(or O)—C  $2^\circ$ ; angles in the base  $3^\circ$ . Symmetry codes are as follows: none *x, y, z*: (i)  $-x, -y, -z$ ; (ii)  $x, -y, \frac{1}{2} + z$ ; (iii)  $-x, y, \frac{1}{2} - z$ ; (iv)  $-x, y, -\frac{1}{2} - z$ ; (v)  $x, -y, -\frac{1}{2} + z$ .

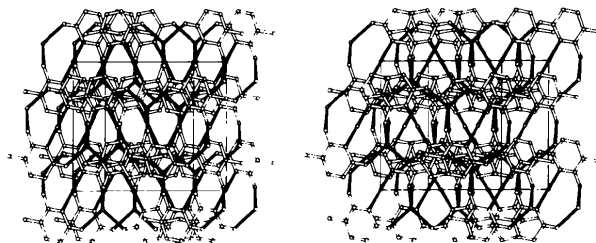


Fig. 2. A stereoview of the crystal packing viewed down the *a* axis, with the *c* axis horizontal, and the *b* axis vertical.

\* Lists of structure factors, anisotropic thermal parameters, and the least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39183 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

case for O(6) of guanine, as illustrated in  $[\text{Cu}_4\text{-(5'-impH}_{-1})_2\text{(phen)}_4\text{(H}_2\text{O)}_4]\text{(NO}_3)_2$  ( $5'\text{-impH}_{-1}$  = the deprotonated form of inosine 5'-monophosphate; phen = 1,10-phenanthroline) in which the O(6)-bonded metal ion is out of the base plane by 1.60 Å (Gellert, Fischer & Bau, 1980).

In general, uracil as well as thymine is a rather poor ligand, compared with other bases like cytosine, adenine, or guanine which all include unprotonated ring N atoms, probably due to the protonation at N(3) [and N(1) in N(1)-unsubstituted uracil or thymine] at pH < 9.5 for uracil and < 9.9 for thymine (Shugar & Fox, 1952). Thus at low or neutral pH, metal bonding to the exocyclic O(4) [and possibly but less so to O(2)] is common for uracil or thymine: examples include  $[\text{Hg}(\text{uracil})_2\text{Cl}_2]$  (Carrabine & Sundaralingam, 1971) and  $[\text{Hg}(\text{dihydrouracil})_2\text{Cl}_2]$  (Carrabine & Sundaralingam, 1971) in which the coordination sites are O(4). However, soft metal ions such as  $\text{Ag}^+$  and  $\text{Pt}^{2+}$ , which have high affinity for N over O, are able to replace a proton at N(3) or N(1) at neutral or even low pH, as exemplified in (1-methylthyminato)Ag [binding sites N(3), O(4), and O(2)] (Guay & Beauchamp, 1979),  $(\text{H}_5\text{O}_2)[\text{Pt}(\text{uracilato})(\text{en})\text{Cl}]\text{Cl}$  [en = ethylenediamine; binding site N(1)] (Faggiani, Lippert & Lock, 1980),  $[\text{Pt}_2(1\text{-methyluracilato})_2(\text{NH}_3)_4](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  [binding sites N(3) and O(4)] (Faggiani, Lock, Pollock, Rosenberg & Turner, 1981),  $[\text{Pt}(\text{thyminato})(\text{en})\text{Cl}]$  [binding site N(1)] (Faggiani, Lippert & Lock, 1980),  $[\text{Pt}_2(1\text{-methylthyminato})_2(\text{NH}_3)_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  [binding sites N(3) and O(4)] (Lock, Peresie, Rosenberg & Turner, 1978),  $[\text{Pt}_2(1\text{-methylthyminato})_2(\text{NH}_3)_4](\text{NO}_3)_2$  [binding sites N(3) and O(4)] (Lippert, Neugebauer & Schubert, 1980),  $\text{Ag}[\text{Pt}(1\text{-methylthyminato})_2(\text{NH}_3)_2](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$  [binding sites Pt-N(3) and Ag-O(4)] (Lippert & Neugebauer, 1980),  $\text{Mn}[\text{Pt}(1\text{-methylthyminato})_2(\text{NH}_3)_2]_2\text{Cl}_2 \cdot 10\text{H}_2\text{O}$  [binding sites Pt-N(3) and Mn-O(4)] (Lippert & Schubert, 1981),  $[\text{Pt}(\text{thyminato})(1\text{-methylcytosine})(\text{NH}_3)_2]\text{ClO}_4$  [binding site N(1)] (Faggiani, Lippert, Lock & Pfab, 1981), and in the present complex. On the other hand, at high pH, metal bonding to the deprotonated N(3) or N(1) is the rule: N(3) coordination in  $[\text{Cd}(\text{uracilato})_2(\text{H}_2\text{O})_3]$  (Mutikainen & Lumme, 1980) and  $[\text{Hg}(1\text{-methylthyminato})_2]$  (Kosturko, Folzer & Stewart, 1974), and N(1) coordination in  $[\text{Ni}(\text{uracilato})_2(\text{H}_2\text{O})_2(\text{NH}_3)_2]$  (Lumme & Mutikainen, 1980) and  $[\text{Cu}(\text{thyminato})(\text{diethylenetriamine})(\text{H}_2\text{O})]\text{Br} \cdot 2\text{H}_2\text{O}$  (Kistenmacher, Sorrell & Marzilli, 1975).

The Ag-N(3) bond length [2.08 (3) Å] is equal to the corresponding one in (1-methylthyminato)Ag and is among the shortest known for similar N donors (Aoki & Saenger, 1984). Comparison of the bond strength between the Ag-O(2) and Ag-O(4) bonds is of interest in connection with the evaluation of the basicity of O(2) and O(4). The higher basicity of O(4) has been widely

suggested, e.g. in (1-methylthyminato)Ag where the Ag-O(4) bond is shorter than the Ag-O(2) bond [2.333 (4) and 2.512 (4) Å] and in (1-methyluracilium)Br where protonation occurs at O(4) rather than at O(2) of the base (Sobell & Tomita, 1964), and this trend is also true for the present complex [Ag-O(4) = 2.40 (3) and Ag-O(2) = 2.51 (2) Å]. A rather fascinating structural feature is the formation of the macrochelate ring  $\text{Ag}(1)\text{-N}(3)\text{-C}(2)\text{-O}(2)\text{-Ag}(2)\text{-O}(4)\text{-C}(4)\text{-N}(3')$ , Fig. 1. Such an Ag-containing eight-membered chelate ring has been repeatedly found in compounds with similar ligands, but with different conformations, i.e. in (1-methylthyminato)Ag, Ag(1-methylcytosine), and in  $[\text{Ag}(\text{adeninium})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  (Gagnon, Hubert, Rivest & Beauchamp, 1977); 1-methylcytosine and adeninium complexes adopt chair and planar conformations, respectively, while 1-methylthyminate and the present complex assume a half-chair form.

The crystal packing, Fig. 2, is largely dominated by the base-base stacking interactions between interpolymer chains, with an average interplanar distance of 3.49 (2) Å, in addition to the intrapolymer ones noted above.

Finally, let us consider possible structures which could be formed in the Ag-polyuridylic acid system at low pH. As noted in *Introduction*, the displacement of one proton indicates  $\text{Ag}^+$  bonding to a deprotonated N(3) site. Thus logically, as shown in Fig. 3, six types of structures can be devised which satisfy the following

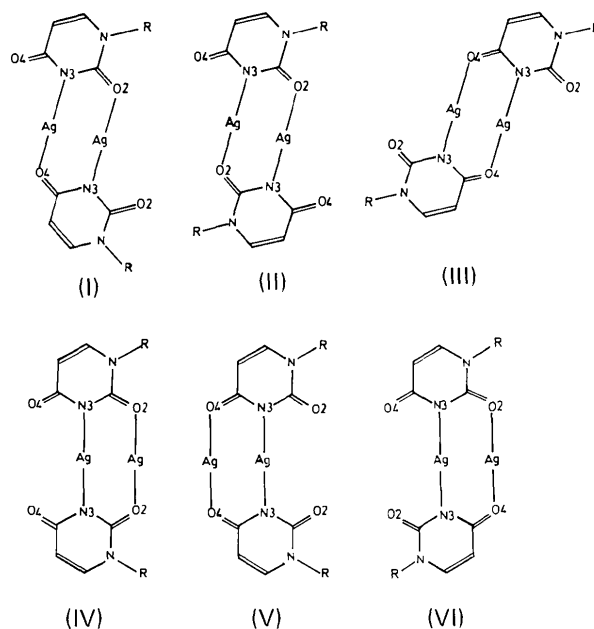


Fig. 3. A schematic representation of the six possible structures for the 1:1 Ag-polyuridylic acid system: (I)-(III) include two N(3)-Ag-O bonds, while (IV)-(VI) include N(3)-Ag-N(3) and O-Ag-O bonds.

requirements: double-helical structures with N(3)—Ag bonding and stoichiometry of one uracil base per silver. The first three, (I)—(III), include two N(3)—Ag—O bonds and the second three, (IV)—(VI), include N(3)—Ag—N(3) and O—Ag—O bonds. In these structures, a marked tendency for Ag<sup>+</sup> to form an eight-membered chelate ring is completely fulfilled. If we neglect O(2) as a candidate for metal bonding because of its low basicity, structures (III) and (V) remain, which are identical with those presented by Guay & Beauchamp (1979). Moreover, there is a distinct possibility of slightly modified structures for (III) and (V), *i.e.* those with the metal-ion bridge between the stacked bases *via* additional Ag—O(4) bonds without major alternation of the stacking geometry, as shown in (1-methyl-thyminato)Ag, Ag(1-methylcytosine), and in the present complex.

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## Structure of Tricarbonylbis(triphenylphosphine)ruthenium(0)—Tetrahydrofuran (2/1), octadecane-7,16-diacetatecopper(II) Methanol Solvate, [Cu(C<sub>16</sub>H<sub>28</sub>N<sub>2</sub>O<sub>8</sub>)]·CuCl<sub>2</sub>·CH<sub>3</sub>OH

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**Abstract.**  $M_r = 606.43$ , monoclinic,  $P2_1/n$ ,  $a = 16.711$  (3),  $b = 9.671$  (2),  $c = 15.829$  (3) Å,  $\beta = 111.00$  (2)°,  $V = 2388.2$  (9) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.687$  (1) Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 4.715$  mm<sup>-1</sup>,  $F(000) = 1248$ ,  $T = 293$  K. Final  $R = 0.078$  for 1877 observed reflections. Both Cu atoms have coordination spheres of irregular octahedral shapes, the first (inside the ligand cavity) being coordinated symmetrically to pairs of N, ether O, and

carbonyl O atoms, the second (of CuCl<sub>2</sub>) to two Cl and four carbonyl O atoms of neighbouring ligands, thus joining the molecules into chains parallel to [101]. Additional complexation by CuCl<sub>2</sub> results in an inequality in N configurations and loss of symmetry in the ligand.

**Introduction.** The structure of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diacetatecopper(II)