ylphosphino)phenyl]phosphonium Tetrafluoroborate (*RR;SS*)-11. A solution of (*RR;SS*-**1**) (0.32 g) in dichloromethane (30 mL) was shaken with aqueous HBF_4 (43% w/w, 1 mL). The organic layer was separated and dried over $MgSO_4$. Filtration, followed by removal of the solvent and recrystallization of the residue from acetone by the addition of dry diethyl ether, afforded the product as colorless rosettes, mp 115-130 °C (0.35 g, 85%). Anal. Calcd for $C_{20}H_{21}BF_4P_2$: C, 58.6; H, 5.2. Found: C, 58.2, H, 5.3. ^1H NMR spectrum in CD_2Cl_2: δ 1.97 (6 H, br s, PMe), 7.01-8.09 ppm (14 H, br m, aromatics) (^+PHP not observed). Conductivity: $\Lambda_M = 23\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1.3×10^{-3} M in $PhNO_2$ at 20 °C).

(−)-*threo*-(*SS*)-11 was prepared as above, but using (*SS*)-**1**, as needles from acetone-diethyl ether, mp 144-146 °C, $[\alpha]_D$ −106° (*c* 0.98, CH_2Cl_2) (78% yield). Anal. Calcd for $C_{20}H_{21}BF_4P_2$: C, 58.6; H, 5.2. Found: C, 58.3; H, 5.2. ^1H NMR spectrum in CD_2Cl_2: δ 1.96 (6 H, br s, PMe), 7.05-8.16 ppm (14 H, br m, aromatics) (^+PHP not observed). Conductivity: $\Lambda_M = 24\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1.1×10^{-3} M in $PhNO_2$ at 20 °C).

***erythro*-(*R;S*)-Methyl[(*S;R*)-2-(methylphenylphosphino)phenyl]-phenylphosphonium Tetrafluoroborate, (*RS;SR*)-11,** was prepared in the same way from (*RS*)-**1** as colorless cubes, mp 123-125 °C (90% yield). Anal. Calcd for $C_{20}H_{21}BF_4P_2$: C, 58.6; H, 5.2. Found: C, 58.6; H, 5.1. ^1H NMR spectrum in CD_2Cl_2: δ 2.11 (6 H, br s, PMe), 7.08-8.0 ppm (14 H, br m, aromatics) (^+PHP not observed). Conductivity: $\Lambda_M = 26\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in $PhNO_2$ at 20 °C).

Dioxides of (*RR;SS*)-1 and (*RS*)-1. (*RR;SS*)-*o*-Phenylenebis-(methylphenylphosphine oxide), (*RR;SS*)-12. A solution of (*RR;SS*)-**1** (0.32 g) in dichloromethane (30 mL) was cooled to 0 °C, treated with aqueous H_2O_2 (30% w/w, 1 mL), and then stirred for 0.25 h. The reaction mixture was dried over $MgSO_4$ and then filtered and the solvent evaporated. The colorless gum crystallized from ethyl acetate (5 mL), after the addition of petroleum ether, as colorless needles, mp 189 °C (0.32 g, 90%). Anal. Calcd for $C_{20}H_{20}O_2P_2$: C, 67.8; H, 5.7. Found: C, 67.8; H, 5.8. ^1H NMR spectrum in $CDCl_3$: δ 2.28 (6 H, d, $^2J_{PH} + {}^5J_{PH}$ = 14 Hz, PMe), 7.06-8.16 ppm (14 H, br m, aromatics).

(+)-(***RR***)-**12** was obtained from (−)-(*SS*)-**1** under similar conditions. It crystallized with difficulty from ethyl acetate in 82% yield as colorless rosettes, mp 197-198 °C, $[\alpha]_D$ +103° (*c* 1.17, CH_2Cl_2). Anal. Calcd for $C_{20}H_{20}O_2P_2$: C, 67.8; H, 5.8. Found: C, 66.8; H, 5.6. ^1H NMR spectrum in $CDCl_3$: δ 2.31 (6 H, d, $^2J_{PH} = {}^5J_{PH}$ = 13.6 Hz, PMe), 7.06-8.10 ppm (14 H, br m, aromatics).

(*RS*)-*o*-Phenylenebis(methylphenylphosphine oxide), (*RS*)-13, was obtained under similar conditions from (*RS*)-**1** as white microcrystals from *n*-butyl acetate, mp 213-215 °C (77%). Anal. Calcd for $C_{20}H_{20}O_2P_2$: C, 67.8; H, 5.7. Found: C, 67.5; H, 5.7. ^1H NMR spectrum in $CDCl_3$: δ 1.90 (6 H, d, $^2J_{PH} + {}^5J_{PH}$ = 14.3 Hz, PMe), 7.37-8.17 ppm (14 H, br m, aromatics).

Acknowledgment. This work was supported by the Australian Research Grants Committee.

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Model Compounds for the Interaction of Silver(I) with Polyuridine. Crystal Structure of a 1:1 Silver Complex with 1-Methylthymine

France Guay and André L. Beauchamp*

Contribution from the Department of Chemistry, University of Montreal, P.O. 6210, Station A, Montreal, Quebec, Canada H3C 3V1. *Received April 18, 1979*

Abstract: The neutralization of uridine in the presence of various quantities of Ag^+ ions has been followed pHmetrically and the data have been interpreted in terms of complexes with 2:1 and 2:2 metal-ligand ratios. The corresponding equilibrium constants have been refined by least squares. Crystals of the 1:1 silver complex with 1-methylthymine (HMT) are monoclinic, space group *C*2/*c*, with a = 11.270 Å, b = 13.239 Å, c = 9.647 Å, and β = 100.11°. The structure was refined on 1004 independent nonzero reflections to an *R* factor of 0.028. One-half of the silver atoms have a linear coordination and bind strongly to N(3) atoms of two deprotonated ligands (Ag-N(3) = 2.081 Å). The resulting planar $Ag(MT)_2^-$ units are connected by the remaining silver atoms, which are tetrahedrally surrounded with oxygen atoms from two $Ag(MT)_2^-$ units. Binding to O(2) is much weaker (Ag-O(2) = 2.512 Å) than with O(4) (Ag-O(4) = 2.333 Å). Those results are discussed in connection with silver binding to poly(U).

It is well established that Ag(I) binds strongly to nucleic acids and polynucleotides.[1] However, there are disagreements in the literature concerning poly(U). Recently, Arya and Yang[2] reported that the UV, ORD, and CD spectra are not affected by silver at neutral pH. On the basis of potentiometric data, UV spectra, and hydrodynamic measurements, Daune, Dekker, and Schachman[3] proposed nonspecific silver binding. On the other hand, UV spectra and pHmetric data obtained by Eichhorn et al.[4] have shown that silver reacts with uracil residues of poly(U) for pH >6. Jensen[5] has identified two types of Ag-poly(U) complexes. The metal first reacts with two uracil residues displacing two protons. In a second step, further fixation of Ag(I) leads to a 1:1 stoichiometry without proton exchange. These reactions are simultaneous for pH ≤7, but resolved at pH 8. Similar conclusions have been reached recently by Klotz and Daune,[6] who also noted that nonspecific binding takes place as well at lower pH and lower silver-to-base ratios.

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Table I. Refined Fractional Coordinates of AgMT ($\times 10^4$, Ag $\times 10^5$, H $\times 10^3$)

atom	*X*	*Y*	*Z*
Ag(1)	0	0	0
Ag(2)	0	11804 (5)	25000
O(2)	1680 (4)	91 (3)	−2211 (4)
O(4)	155 (3)	2284 (3)	655 (4)
N(1)	2057 (4)	1788 (3)	−2424 (5)
N(3)	886 (4)	1185 (3)	−804 (4)
C(1)	2824 (7)	1575 (6)	−3483 (8)
C(2)	1539 (4)	973 (4)	−1821 (5)
C(4)	705 (4)	2142 (4)	−354 (5)
C(5)	1164 (4)	2956 (3)	−1051 (5)
C(6)	1828 (5)	2748 (4)	−2045 (6)
C(7)	881 (7)	4008 (5)	−661 (8)
H(6)	220 (6)	325 (5)	−248 (8)
H(11)	354 (7)	128 (5)	−297 (8)
H(12)	243 (9)	119 (7)	−436 (11)
H(13)	315 (7)	217 (6)	−390 (8)
H(71)	−1 (7)	415 (5)	−91 (7)
H(72)	140 (9)	445 (7)	−78 (10)
H(73)	106 (6)	416 (5)	34 (8)

In order to cast more light on the reactions of silver with uracil moieties, we have reexamined the Ag–uridine system. We have extended a previous pHmetric study by Eichhorn et al.[4] using a wider range of concentrations to determine the stoichiometries and stabilities of the species formed. Attempts to isolate solid samples of the complexes identified in solutions failed, but a 1:1 complex was obtained with the related ligand 1-methylthymine and its crystal structure is reported here.

Experimental Section

Potentiometric Measurements. The pH data were collected at 25 °C using a locally made digital pH meter and a system consisting of a glass electrode and a two-junction calomel electrode with 0.1 M KNO_3 in the outside jacket. Overall reproducibility is estimated to ±0.015 pH unit. Samples (100 mL) containing 0.0190 M HNO_3, 0.0220 M uridine (Aldrich Co.), and various amounts of $AgNO_3$ were titrated with carbonate-free 0.948 M NaOH. No supporting electrolyte was used and ionic strength ranged from 0.03 to 0.06 for the data used hereafter.

Preparation of AgMT. 1-Methylthymine (0.14 g, 1 mmol) (HMT, Het-Chem) was dissolved in ~50 mL of warm water and 1.0 mL of 1.0 M $AgNO_3$ solution was added. After addition of 1.0 mL of 1.0 M NaOH, a quantitative yield of AgMT was obtained as a white powder from the cooled mixture. To grow crystals, neutralization was made with concentrated ammonia (instead of NaOH) until the precipitate initially formed redissolved. Upon slow evaporation of NH_3, well-formed, colorless crystals were obtained. They darken slowly on exposure to daylight for several days.

Crystal Data. $C_6H_7AgN_2O_2$, mol wt 247.0, monoclinic, space group $C2/c$, a = 11.270 (4) Å, b = 13.239 (2) Å, c = 9.647 (3) Å, β = 100.11 (3)°, V = 1417.0 Å^3, d_0 = 2.30 (2) g cm^{-3} (flotation in bromobenzene-bromoform), d_c = 2.315 g cm^{-3}, Z = 8 monomers per cell, μ(Mo Kα) = 27.8 cm^{-1}, λ(Mo K$\bar{\alpha}$) = 0.710 68 Å (graphite monochromator), t = 25 °C.

Crystallographic Measurements and Structure Resolution. The crystal selected for data collection had dimensions 0.10 × 0.12 × 0.17 mm.[3] A set of precession photographs showed monoclinic symmetry and indicated space group Cc or $C2/c$. The crystal was mounted on an Enraf-Nonius CAD4 diffractometer and the cell parameters were obtained from least-squares fit of the setting angles for 25 reflections centered in the counter aperture. The intensity data were collected using the $\omega/2\theta$ scan technique. A fixed slit of 4 × 4 mm^2 was used and the scan range (ω) was $(1.30 + 0.347 \tan \theta)°$ extended 25% on either side for backgrounds. Scan speed between 16.7 and 1.0 deg min^{-1} was automatically selected to make $I/\sigma(I) = 100$, but a maximum scan time of 120 s was imposed. Prescans at 16.7° min^{-1} were done and all reflections having $I/\sigma(I) < 1$ were labeled weak and not remeasured. Three standard reflections were used as a check on instrument and crystal stability, and showed only random fluctuations. Crystal orientation was checked every 100 reflections by recentering 3 reflections. If a difference >0.1° was found between the scattering vectors and the direction deduced from the orientation matrix, automatic recentering and least-squares refinement on the 25 reflections were carried out to define a new matrix.

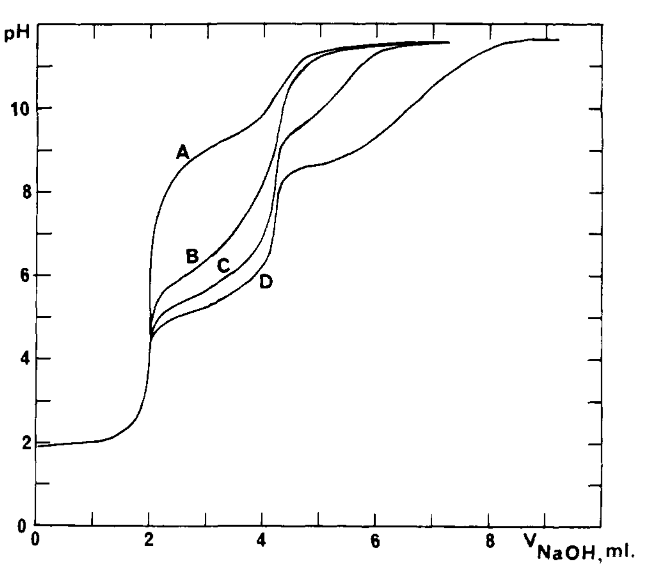


Figure 1. pHmetric titration curves with 0.948 M NaOH. The 100-mL samples contained 0.0190 M HNO_3 and 0.0220 M uridine with the following concentrations of $AgNO_3$: A = 0, B = 0.0101 M, C = 0.0202 M, and D = 0.0358 M.

A total of 1258 hkl and $hk\bar{l}$ reflections in a sphere of $2\theta \le 50°$ were measured. Net intensity I and esd $\sigma(I)$ were calculated as described previously.[13] A set of 1004 reflections with $I \ge 2.5\sigma(I)$ was retained for structure determination. An absorption correction was applied (Gaussian integration, grid 10 × 10 × 10, transmission coefficient 0.70–0.80) and the data were corrected for Lp.

The structure was solved by the heavy-atom method and refined on F by full-matrix least squares. The statistical distribution of the normalized structure factors clearly favored the centric space group $C2/c$. From a Patterson map, the eight Ag atoms were found to occupy two special positions. A Fourier map easily revealed the positions of all nonhydrogen atoms. However, since the free ligand has a pseudo-twofold axis through N(3) and C(6), there remained an ambiguity in identifying N(1) and C(5). The higher peak on the map was assigned to N(1), but as a check the alternative choice was refined as well. The solution retained is believed to be correct for the following reasons: (1) Refinement (Ag anisotropic, remaining nonhydrogen atoms and H(6) isotropic) led to an R factor $(=\sum(|F_o| - |F_c|)/\sum|F_o|)$ of 0.042, compared to 0.043 for the alternate model. (2) The temperature factors of N(1) and C(5) (B = 2.16 and 2.84 Å^2) compare well with those of C(2), N(3), C(4), C(6) (2.16, 2.24, 2.34, 2.52 Å^2). With the other model, the four last values are similar, but those of N(1) and C(5) become 3.38 and 1.79 Å^2, respectively. (3) Bond lengths C(4)–C(5) and N(1)–C(2) (1.394 and 1.415 Å) are in the same order (although not equal, probably owing to Ag coordination) as in the free ligand (1.372, 1.432 Å). That order would be reversed for the other alternative.

A disordered model in group $C2/c$ or an ordered structure in group Cc (which would appear to be disordered when refined in $C2/c$) is ruled out by the low and constant values of the temperature factors of the ring atoms. Indeed, since atomic positions in the two halves related by the pseudo-twofold axis are not perfectly superimposable, forcing them to be superimposed should result in high and irregular temperature factors.

At the latest stage of the refinement, all nonhydrogen atoms were anisotropically refined. The hydrogen atoms were located on a ΔF map and they were isotropically refined. In the last cycles, individual weights $w = 1/\sigma(F)^2$ based on counting statistics were used. The final agreement factors are R = 0.028 and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 0.037. The final ΔF map showed maximum peaks of 0.37 e Å^{-3} near Ag atoms.

The refined coordinates are shown in Table I. Lists of temperature factors and of structure amplitudes are part of the supplementary

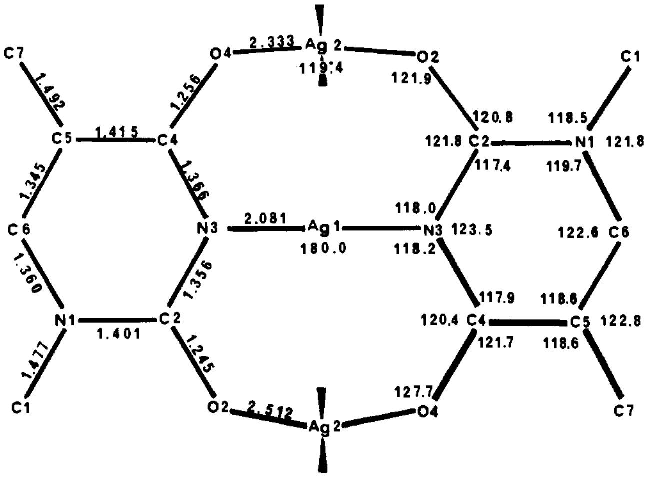


Figure 2. Interatomic distances and bond angles in AgMT. Ag(1) occupies a crystallographic inversion center. The esd's follow: Ag-O(N), 0.004; C-C(N,O), 0.006-0.007 Å; O-Ag-O, 0.1°; Ag-N(O)-C, 0.3°; angle involving C, N, O = 0.4°.

material. The form factors used were those of Cromer and Waber,[7] except for hydrogen.[8] The scattering curve of Ag was corrected for anomalous dispersion.[9]

Results and Discussion

Potentiometric Study. Neutralization curves are shown in Figure 1. Uridine has no appreciable basic properties even at pH 2 and the strongly acidic protons from HNO_3 are neutralized by the first 2 mL of each curve. Between 2 and 4 mL, curve A, weakly acidic H(3) is titrated. The data in that interval were used to refine pK_a of uridine (HU), using program SCOGS by Perrin and Sayce.[10]

$$HU \rightleftharpoons H^+ + U^- \quad k_a = [H^+][U^-]/[HU] \qquad (1)$$

That program refines the logarithm of equilibrium constants by minimizing $\sum(V_o - V_c)^2$, where V_o and V_c are the observed and the calculated volumes of NaOH added, respectively. A good fit was obtained [$\Delta_V = \sum|V_o - V_c|/n = 0.034$ mL and $\sigma_V\ [|V_o - V_c|^2/(n-1)]^{1/2} = 0.030$ mL] and the refined value 9.11 (1) is in good agreement with earlier results.[11]

In curves B, C, and D, Ag^+ clearly displaces uridine protons, which are titrated at a much lower pH than in the free ligand. The interesting feature of curve B is that 2 mol of uridine protons is displaced by only 1 mol of Ag^+ ions, indicating a 1:2 reaction:

$$Ag^+ + 2HU \rightleftharpoons AgU_2^- + 2H^+ \qquad (2)$$

Equilibrium 2 was redefined as a conventional formation reaction (3) and attempts were made to refine β_{12} using the data between $V = 2$ and 4 mL of the three curves.

$$Ag^+ + 2U^- \rightleftharpoons AgU_2^- \quad \beta_{12} = [AgU_2^-]/[Ag^+][U^-]^2 \quad (3)$$

It became obvious that a metal-rich species was also present and a 1:1 equilibrium was introduced.

$$Ag^+ + U^- \rightleftharpoons AgU \quad \beta_{11} = [AgU]/[Ag^+][U^-] \quad (4)$$

Refinement led to the following results: log $\beta_{11} = 5.2$ (1), log $\beta_{12} = 9.4$ (2), $\sigma_V = 0.13$ mL, $\Delta_V = 0.11$ mL. However, when the curves were refined independently, β_{12} remained constant whereas β_{11} drifted regularly indicating that polynuclear species are formed. The metal-rich species was assumed to be dimeric:

$$2Ag^+ + 2U^- \rightleftharpoons Ag_2U_2 \quad \beta_{22} = [Ag_2U_2]/[Ag^+]^2[U^-]^2 \quad (5)$$

Refinement of β_{12} and β_{22} on the three curves together or separately gave the same results: log $\beta_{12} = 9.3$ (1), log $\beta_{22} = 12.2$ (1), $\sigma_V = 0.07$ mL, and $\Delta_V = 0.05$ mL. The latter model is retained. Refinement of an extra constant for an Ag_3U_2 complex was attempted. After many cycles, it had become very small and was still decreasing, whereas β_{12} and β_{22} were not affected. Consequently, fixation of a third Ag^+ ion does not take place. A small amount of monomeric AgU may be present, but the limited range of $AgNO_3$ concentrations used precludes simultaneous refinement of 1:1 and 2:2 species.

Distribution curves show that, in the present conditions, Ag_2U_2 is the predominant species for pH <6: it is ≥ four times as abundant as AgU_2^-, whatever initial metal-ligand ratio was used. Above pH 6, AgU_2^- becomes increasingly important and remains stable, as evidenced from the absence of Ag_2O precipitation beyond $V = 4$ mL, curve B. Precipitation does occur for curve C and D, but the position of the last end point shows that those Ag^+ ions used to form quantitatively AgU_2^- escaped precipitation.

Both Ag complexes detected here are very soluble in water. Upon evaporation, the solution remained clear until the volume was considerably reduced; then some decomposition occurred with formation of what appeared to be metallic silver. This phenomenon was not further investigated.

Description of the Crystal Structure. Optimum use is made of the three donors (N(3), O(4), and O(2)) on each methylthymine ligand (Figure 2). Ag(1) occupies a crystallographic inversion center and its coordination is perfectly linear. Both Ag-N(3) bonds (2.081 Å) are equal and among the shortest known. Much greater bond lengths have been reported for similar nitrogen donors such as imidazole (2.12 Å),[12] adenine (2.15 Å),[13] and methylcytosine (2.225 Å).[14] Short metal-N(3) bonds have also been found for methylthymine compounds with mercury[15] and platinum.[16]

In the planar $Ag(MT)_2^-$ unit, two pairs of carbonyl oxygens are brought into a suitable orientation to coordinate to Ag(2). Each Ag(2) atom is shared between two $Ag(MT)_2^-$ units providing a tetrahedral environment of oxygens (Figure 3). The Ag-O(4) distance (2.333 Å) is similar to the one found in $AgNO_3$·methylcytosine (2.367 Å).[14] The greater Ag(2)-O(2) distance (2.512 Å) reflects the lower basicity of O(2). Reduced donor ability of O(2) compared to O(4) has been predicted from theoretical calculations[17] on free thymine and the same conclusions probably hold when H(3) has been substituted by silver. It is noteworthy that O(4) was found to be bonded while O(2) was free in $[Pt_2(NH_3)_4(MT)_2](NO_3)_2 \cdot H_2O$.[16]

The packing diagram (Figure 3) shows that stacking effects are important in stabilizing the crystal. The distance (~3.5 Å) between pairs of parallel methylthymine ligands is as expected and all nonbonded contacts are normal.

Discussion

Potentiometric experiments have shown that AgU_2^- is the stable complex species at high pH. Crystals of the methylthymine compound contain $Ag(MT)_2^-$ units in which very strong Ag-N(3) bonds are found. Linear two coordination and greater affinity for N donors than for O donors are general features of silver coordination chemistry. For those reasons, it is very likely that silver is linearly coordinated to N(3) in AgU_2^- as well (I).

The crystal structure suggests that AgU_2^- could accept as many as two extra Ag^+, each using one of the available pairs of carbonyl oxygens. However, this would lead to an $Ag_3U_2^+$ species in solution and our results provide no evidence for an Ag/U ratio >1. Thus, it appears that AgU_2^- accepts only one Ag^+ and we have retained two tentative structures for Ag_2U_2 on the basis that Ag^+ should bind to N(3) and O(4). Less basic O(2) is not considered for the reasons given earlier. Structure II contains a two-silver eight-membered ring of the type reported for a silver-methylcytosine complex.[14] Structure III retains the strong N(3)-Ag-N(3) sequence and a more weakly bonded Ag atom would be found between two O(4) oxygens brought to the same side of the molecule.

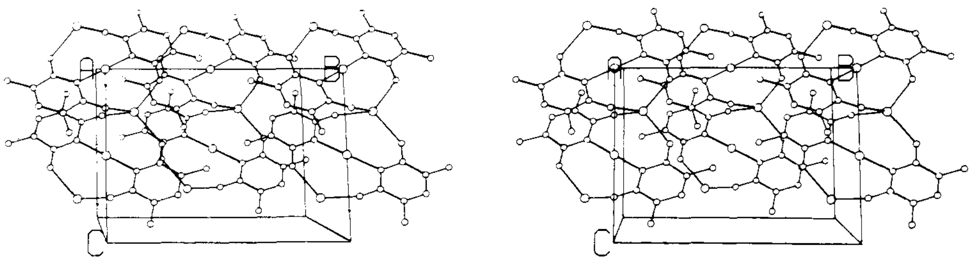
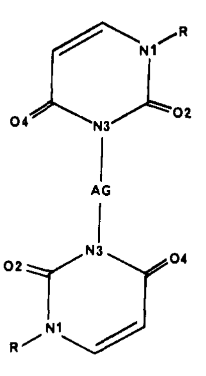


Figure 3. Packing diagram of AgMT.



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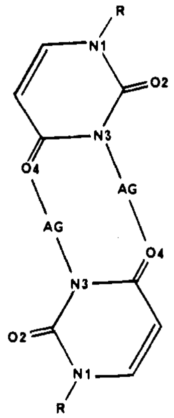

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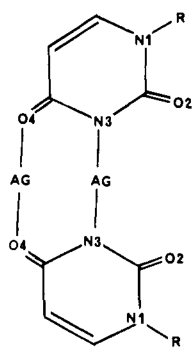

III

The formation constants obtained earlier were used to calculate binding profiles at fixed pH (i.e., number of Ag^+ bound per ligand vs. log (free Ag^+)). It is found that, for pH 8 and a total uridine concentration of 0.01 M, for instance, silver reacts in two separate steps: at low Ag^+ content, AgU_2^- is first formed, displacing two protons, and at higher Ag^+ concentrations, further fixation takes place without proton exchange. For pH 7 and 6, the two steps overlap. Comparison of these results with those reported by Jensen[5] for poly(U) shows that silver reacts more strongly (i.e., at a lower log (Ag^+)) with poly(U), but the reaction pattern is the same in both cases. It is tempting to relate the closeness in reactivity pattern to a similarity in the structures of the species formed. Jensen has proposed for the first complex a structure of type I, in which two uracil residues from different chains or from the same bent chain are brought together in such a way that Ag^+ is linearly coordinated to two properly positioned N(3) atoms. The present work clearly supports this model, which explains the ordered configuration indicated by the melting curves of Ag-poly(U) complexes.[5] No model was proposed for the second reaction leading to a 1:1 ratio. Assuming that the ordered structure is maintained, structures II and III may be considered as reasonable models because they would readily form with minimum readjustment when the N(3)-Ag-N(3) bridges already exist. Indeed, III would be preferred if both O(4) carbonyl groups are on the same side. It is analogous to the binding mode found with platinum in the synthetic α-pyridone blue.[18] If O(4) atoms are on opposite sides, II would form by slippage of the uracil residues in the plane with respect to each other. In the latter process, one of the Ag-N(3) bonds of I would have to break and be replaced by an Ag-O(4) bond, while a similar process would close the eight-membered ring.

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Supplementary Material Available: Temperature factors and structure factors with standard deviations (6 pages). Ordering information is given on any current masthead page.

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