Nucleic Acid–Metal Interactions. 2. Complexes of Silver(I) with Guanosine and 7-Methylguanine from Studies of Isotropic and Dichroic Spectra†

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Attempts to characterize nucleic acid–silver complexes have directed attention to questions about how the free nucleic acid bases interact with silver ions in dilute aqueous solution. Studies of isotropic UV and IR absorbance, and linear dichroism in oriented polymer matrices, together with molecular orbital calculations, lead to the conclusion that both guanosine and 7-methylguanine form dimeric species upon interaction with Ag^+ in neutral solution, however, with different structures. With guanosine the complexation most likely involves the replacement of the enolic proton by silver and the simultaneous coordination of the silver to the N(7) nitrogen of a second guanosine molecule. The silver ion in the 7-methylguanine complex most probably displaces the N(1) proton and coordinates to the keto oxygen of the second 7-methylguanine group. The results obtained should be of considerable help toward elucidating the structural changes brought about by the silver ions in nucleic acids and polynucleotides.

Introduction

Upon interaction with silver ions the structures of nucleic acids change[1-6] as revealed particularly clearly by dichroic spectral measurements, such as, the circular dichroism,[7,8] electric dichroism,[9,10] and flow dichroism[11] of the appropriate solutions; however, just what these structural changes are cannot, as yet, be answered. We have begun work, for this reason, on the interaction of silver ions with purine and pyrimidine derivatives since the ring nitrogens of the heterocyclic bases in nucleic acids are thought to be the principal silver ion binding sites.[12] We hope that as a result of these studies it may become possible to infer the structures of nucleic acid–silver ion complexes.

This particular report is concerned with the silver ion complexes of guanosine and of 7-methylguanine. The first of these compounds represents one of the "monomers" of nucleic acids; the choice of the second compound was dictated by some evidence of the involvement of the N(7) nitrogen of the purine moiety in the complexing of silver ions.[13] Results of solution spectra are combined in the work to be presented here with linear dichroism of samples oriented in stretched polymer matrices and with molecular orbital calculations in order to derive self-consistent models for the relevant complexes.

Experimental Section

7-Methylguanine (7MG) and guanosine (Gs) were purchased from Sigma Chemical Co. and were used without further purification. All other chemicals used were of reagent grade.

Poly(vinyl alcohol), PVA, films containing the samples were prepared by mixing 10% aqueous PVA and the calculated quantity of about 10^{-3} mol dm^{-3} solutions of the appropriate guanine derivative, followed by the addition of the required amount of silver ions slowly and with constant stirring at about 50 °C. The resulting homogeneous solution was spread onto a horizontal glass plate and kept for several days in a closed chamber to give an isotropic film with a water content just above 7% w/w. Reference films without the addition of guanine derivatives were prepared under indentical conditions.

Films containing relatively high concentrations of silver were found to lose water and become colored on standing. This effect appears to be irreversible; it is not prevented by protection of the samples from light, and the absorption band associated with this silver–PVA complex shows very pronounced linear dichroism upon stretching. For these reasons the data reported here are restricted to films where the molar ratio of silver to the guanine derivative did not exceed 1.5; under these circumstances we found no evidence for any interaction between silver ions and the PVA matrix.

We found that reproducibility of the solution spectral results could also be improved if solutions were mixed at temperatures near 50 °C and the measurements were then taken at room temperature several hours after the solution preparation.[14]

The spectrophotometers used were a Jasco J-500 spectropolarimeter, a Cary 219 UV–visible spectrophotometer, and a Nicolet MX-1 Fourier transform infrared spectrometer. The method of measuring UV dichroic spectra has been described;[15] at a wavelength λ the dichroic absorbances corrected for background are denoted by $A_{\parallel}(\lambda)$ and $A_{\perp}(\lambda)$, corresponding to the use of incident light polarized parallel and perpendicular, respectively, to the stretch directions of the films. Polarization of the infrared source was achieved by means of an IGP 225 grid polarizer. Absorbances were calculated from transmittances measured separately for sample and for reference films.

All linear dichroic data reported here refer to films with the stretch ratio of $R_s = 4.3$.

Results

Solution Studies. Figure 1 shows selected absorption spectra of guanosine in the presence of various amounts of silver ion of pH 7 in 0.001 mol dm^{-3} cacodylate buffer solution. The numbers labeling the curves correspond to the molar ratios of stoichiometric silver ion to guanosine concentration; the concentration of guanosine was held constant at 7.9×10^{-5} mol dm^{-3}. The solutions were buffered since binding of silver ions to guanosine is known

† For part 1 in this series, see ref 11.

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TABLE I: Resolution of Absorption Spectra into Harmonic Progressions[a,b]

	transition I		transition II		
	$\tilde{\nu}_{00}$, cm^{-1}	X	$\tilde{\nu}_{00}$, cm^{-1}	X	b_g, cm^{-1}
guanosine	35 430 (30)	1.30 (0.05)	39 060 (50)	1.30 (0.05)	1020 (20)
guanosine-Ag	32 950 (30)	1.42 (0.06)	35 620 (60)	1.61 (0.05)	1010 (20)
7-methylguanine	34 150 (30)	1.27 (0.05)	39 740 (50)	1.15 (0.05)	1020 (20)
7-methylguanine-Ag	33 120 (80)	1.84 (0.10)	37 440 (150)	2.32 (0.15)	980 (60)

[a] The separation between the bands was fixed at $V = 1480$ cm^{-1}. [b] The figures in brackets are the linear estimates of the standard deviations.

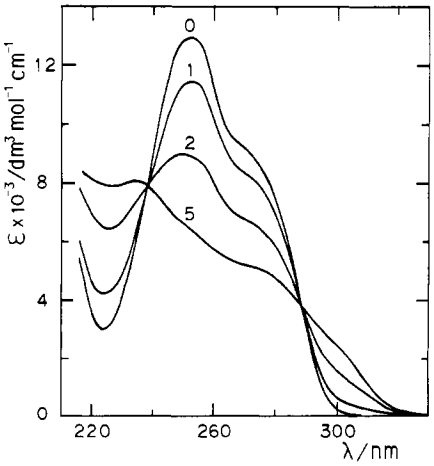

Figure 1. Absorption spectra of guanosine in the presence of various amounts of silver ion in 0.001 mol dm^{-3} cacodylate buffer solution. Each number corresponds to the molar ratio of stoichiometric silver ion to guanosine concentration.

to liberate protons.[13] The presence of isosbestic points indicates that two spectroscopically significant species are present only. These may be identified as free guanosine and a silver–guanosine complex containing silver and guanosine in 1:1 molar ratio.[13] If we denote the molar ratio of total and of bound silver to guanosine in solution by β and r, respectively, and the constant concentration of guanosine by a, the expression for equilibrium leads to

$$r^2 - \left(1 + \beta + \frac{1}{Ka}\right) r + \beta = 0 \qquad (1)$$

where K is the stability constant. The value of r is given by $r = (A_\beta^\lambda - A_0^\lambda)/(A_\infty^\lambda - A_0^\lambda)$ where A_0^λ, A_β^λ, and A_∞^λ refer to the absorbances at a wavelength λ of solutions containing no silver, silver in the ratio β, and no free guanosine, respectively. Least-squares fit of the data to this equation provides the values A_∞^λ and of the stability constant, found to be $K = (1.6 \pm 0.1) \times 10^4$ mol^{-1} dm^3.

Figure 2 shows the analysis of the spectra of guanosine and of its silver complex in terms of harmonic progressions of a single vibrational mode.[16] For each transition the intensity, $I(\tilde{\nu})$, as a function of the wavenumber $\tilde{\nu}$, is given by

$$I(\tilde{\nu}) = \sum_{m=0} (I_{00} X^m / m!) \exp\{-4 \ln 2[b_g^{-2}(\tilde{\nu} - \tilde{\nu}_{00} - mV)^2]\} \qquad (2)$$

Here the parameters of the least-squares fit have direct physical significance: they are the intensity, I_{00}, and the position, $\tilde{\nu}_{00}$, of the 0,0 band, the Gaussian bandwidth, b_g, and the ratio of 1,0 to 0,0 band intensities, X. The quantity V, representing the separation between the harmonic bands, was taken to be 1480 cm^{-1}, the value of the most intense band in the Raman spectrum of guanosine.[17] We introduced the additional restriction into the curve-fitting procedure of assuming that b_g is the same for all transitions within a given absorption envelope. The resolution of the experimental spectrum of guanosine into two transitions above 220 nm shown in Figure 2a is unique within the limitations of

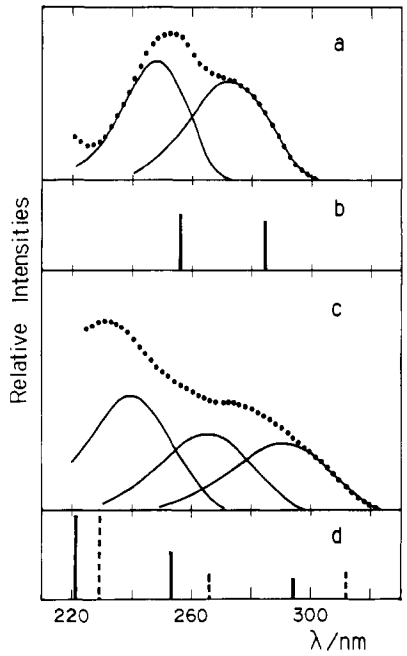

Figure 2. Resolution of the observed spectra (···) of guanosine (a) and guanosine–silver complex (c) into vibronic progressions by means of eq 2. The corresponding line spectra indicate SCF MO calculation for guanosine (b), enolic form of guanosine (broken vertical lines d), and cationic form of guanosine (full vertical lines in d).

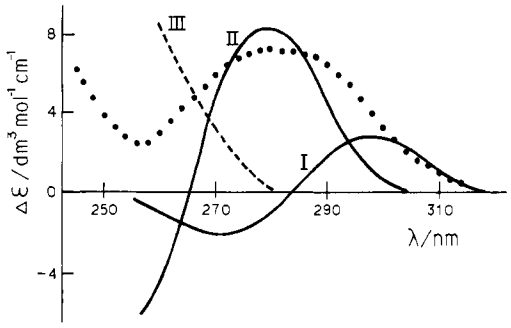

Figure 3. Circular dichroism spectrum (···) of guanosine–silver complex (molar ratio $\beta = 1.5$) in 0.001 mol dm^{-3} cacodylate buffer solution. Solid and broken curves refer to the calculated exciton spectra for the transitions I, II, and III (see Discussion for details).

the model and the fitting parameters are collected in Table I. In the case of the silver complex the region in question includes three transitions and their resolution into the individual spectra is less precise. For this reason the interpretations of the fitting parameters, also included in Table I, are less certain although the overall shapes, positions, and magnitudes of the resolved transitions shown in Figure 2c may be taken to be essentially correct. The line spectra in Figure 2, b and d, have been calculated by means of π-electron SCF MO calculations with CI involving all first-excited states.[18] Details and the significance of these results will be considered in the Discussion section.

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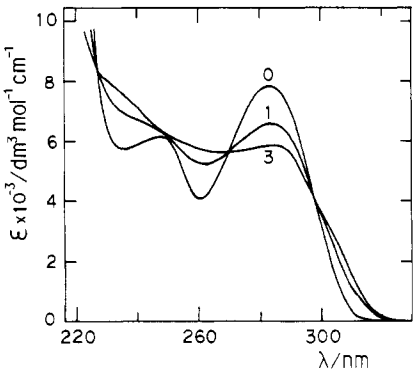

Figure 4. Absorption spectra of 7-methylguanine in the presence of various amounts of silver ion in 0.001 mol dm^{-3} cacodylate buffer solution. Each number corresponds to the molar ratio of total silver to 7-methylguanine.

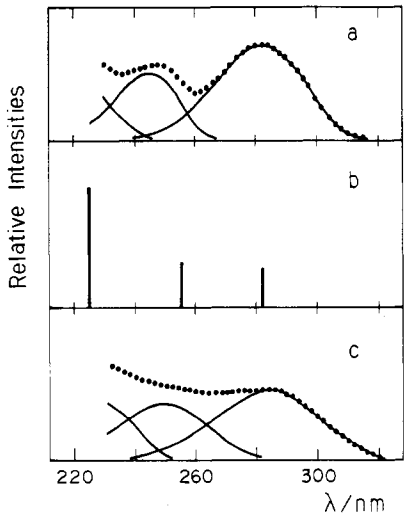

Figure 5. Resolution of the observed spectra (···) of 7-methylguanine (a) and 7-methylguanine–silver complex (c) into vibronic progressions by means of eq 2. The line spectrum in (b) indicates SCF MO calculation for 7-methylguanine.

The guanosine solutions show in the presence of silver ions very pronounced circular dichroism as shown in Figure 3 by dotted curve. It should be observed that the $\Delta\epsilon$ values are an order of magnitude larger than those for guanosine itself.[19] The significance of the curves drawn by solid and broken lines in this figure will be explained in the Discussion.

As also with guanosine, upon addition of silver ions to 7-methylguanine solutions protons are liberated. In Figure 4 the absorption spectra of 7-methylguanine and selected solutions containing added silver ions are shown in 0.001 mol dm^{-3} cacodylate buffer. The concentration of 7-methylguanine was held constant at 7.9×10^{-5} mol dm^{-3} and the numbering of the curves corresponds to β, the molar ratio of total silver to 7-methylguanine in solution. It is again permissible to analyze the data in terms of two spectroscopic species only, the free 7-methylguanine and its silver complex. We derived a series of expressions for various assumed values of the silver to purine ratio in the complex and tested these by means of least-squares fits against the absorbance data at a series of wavelengths. Unequivocally these tests resulted in the conclusion that the complex is formed in a 1:1 molar ratio with a stability constant of $(1.9 \pm 0.1) \times 10^4$ mol^{-1} dm^3.

The resolution into vibronic progressions of the spectra of 7-methylguanine and its silver complex is shown in Figure 5, a and c, and the relevant fitting parameters are included in Table I. The theoretical line spectra shown in Figure 5b will be referred to and discussed later.

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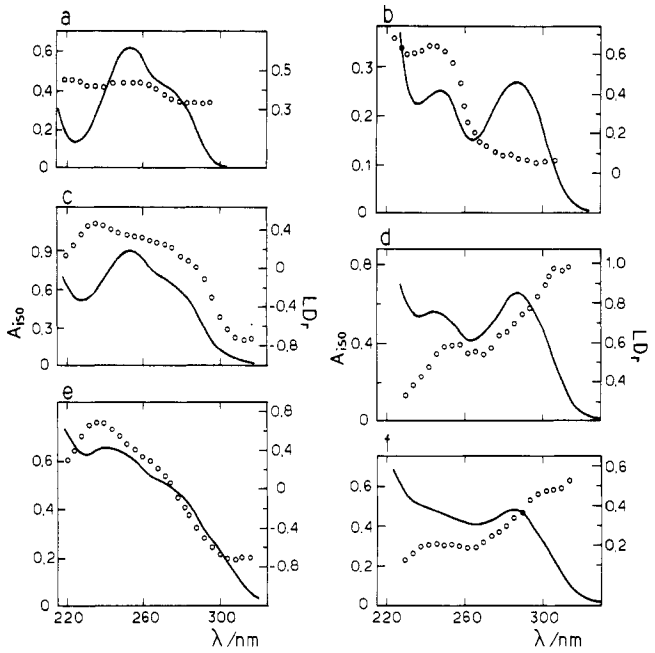

Figure 6. Calculated isotropic spectra (A_{iso}, —) and reduced dichroism curves (LD_r, ooo) of guanosine (a, c, e) and 7-methylguanine (b, d, f) at various amount of silver ion in stretched PVA film (R_s = 4.3). (a), (c), and (e) guanosine–silver at β = 0, 0.5 and 1.0, respectively. (b), (d), and (f) 7-methylguanine–slver at β = 0, 0.5, and 1.5.

TABLE II: Assignment of Observed Infrared Bands in PVA Films

	C(6)-O stretch/ cm^{-1}	NH_2 bending/cm^{-1}	N(3)-C(4) stretch/ cm^{-1}
guanine	1710	1640	1615
guanosine	1685	1645	1605
7-methylguanine	1675	1640 (shoulder)	1595

Studies in a PVA Matrix. 1. UV Region. In Figure 6 are shown the calculated isotorpic absorbances, A_{iso}, and the reduced dichroism, LD_r

$$A_{iso} = (A_{\parallel} + 2A_{\perp})/3 \qquad LD_r = (A_{\parallel} - A_{\perp})/A_{iso} \quad (3)$$

in stretched poly(vinyl alcohol) films of guanosine and of 7-methylguanine in the absence of silver ions (Figure 6, a and b) and in the presence of silver ions, β = 0.5 to 1.5 (Figure 6c–f). Comparison of the isotropic spectra with the relevant solution spectra shown in Figures 1 and 4 indicates that the absorbing species in solution and in the PVA films may be taken to be identical. In addition, the linear dichroism spectra are consistent with the interpretation of the experimental solution spectra in terms of the separate transitions shown in Figures 2 and 5. If, as supposed, the dominant vibrational progression in each transition is one that involves a totally symmetrical vibration mode, then the reduced dichroism should be constant and its magnitude determined by the orientation of the transition moment of the *electronic* transition. In accordance with this expectation the linear dichroism values, shown in the Figure 6, are approximately constant in the regions where the overlap between the resolved progressions may be regarded as negligible.

2. Infrared Region. In Figure 7 are shown the infrared dichroic spectra in stretched PVA films of guanosine and 7-methylguanine in the absence of silver (Figure 7, a and b) and with silver present at β = 0.5 to 1.5 (Figure 7c–f). In the same region the spectrum of guanine in PVA films shows three distinct bands, the assignments and wavenumbers of which[20] are shown in Table II together with the corresponding data for guanosine and 7-methylguanine.

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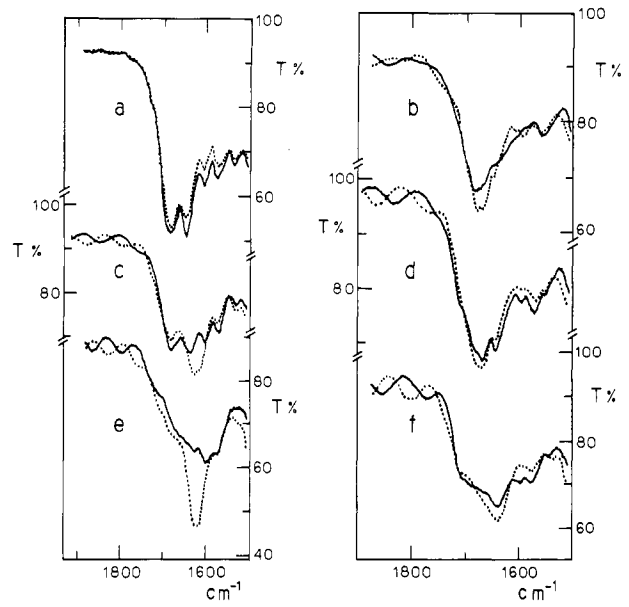

Figure 7. Infrared dichroic spectra ($T_{\parallel}$, —— and $T_{\perp}$, ···) of guanosine (a, c, e) and 7-methylguanine (b, d, f) at various amount of silver ion in stretched PVA film (R_s = 4.3). (a), (c), and (e) guanosine–silver at β = 0, 0.5, and 1.0, respectively. (b), (d), and (f) 7-methylguanine–silver at β = 0, 0.5, and 1.5.

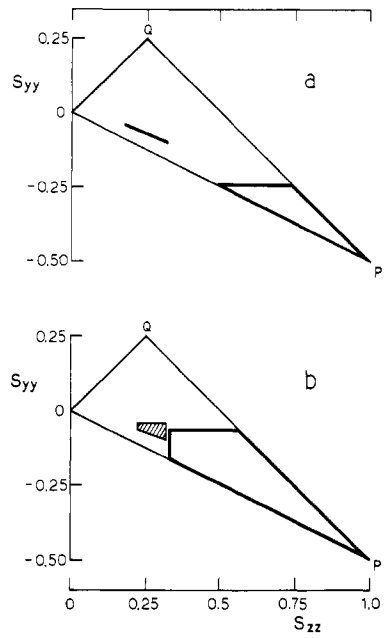

Figure 8. Orientation triangle OPQ drawn for two orientation factors S_{zz} and S_{yy}. (a) Range of permissible values of S_{zz} and S_{yy} for guanosine (solid line) and for guanosine–silver complex (area surrounded by thick solid lines). (b) Most likely region of S_{zz} and S_{yy} for 7-methylguanine (shaded area) and for 7-methylguanine–silver complex (area surounded by thick solid lines).

The sign and magnitude of the reduced dichroism of the three bands for guanine[21] and guanosine compare well which indicates that the chromophores orient in the stretched films in a very similar manner. However, the orientation direction of 7-methylguanine is significantly different from that of guanosine as evidenced, for example, by a comparison of the signs of the LD_r values of the C=O stretching vibrations (Figure 7, a and b).

3. Orientation Factors. Generally the orientation of a planar molecule may be described by just three orientation factors, denoted by S_{xx}, S_{yy}, and S_{zz}, in a properly chosen molecular coordinate system with axes labeled such that $S_{xx} \leq S_{yy} \leq S_{zz}$ is fulfilled. The z axis in this system is referred to as the orientation axis and the x axis is perpendicular to the molecular plane. Because of the relation $S_{xx} + S_{yy} + S_{zz} = 0$ there are only two independent orientation factors.[22]

The numerical magnitudes of the orientation factors give a clear indication about the extent to which each of the three axes in this system is correlated with the direction of stretch. Their significance is well illustrated by the use of orientation triangles[23] shown in Figure 8 where the two independent orientation factors are chosen to be S_{yy} and S_{zz}. For rods $S_{xx} = S_{yy}$ and thus their orientation is represented by the line OP; for disks, $S_{yy} = S_{zz}$ which corresponds to the line OQ. Along PQ the correlation between the x axis and the stretch direction is perfect and the lines S_{xx} = constant are parallel to PQ.

For an in-plane transition whose moment subtends an angle θ with the z axis the following relation holds:

$$LD_r = 3(S_{yy} \sin^2 \theta + S_{zz} \cos^2 \theta) \quad (4)$$

There are three unknowns, θ, S_{yy}, and S_{zz}, and for a solution one requires the reduced dichroism of three *independent* transitions whose moments have known directions relative to an arbitrary molecule-fixed coordinate system; a condition that is rarely fulfilled.

Meaningful values for the three unknowns may be obtained, nevertheless, by setting up inequalities restricting the possible range of the orientation factors.[21,24] Thus, for example, it follows that

$$S_{yy} \leq \tfrac{1}{3}LD_r^{min} \qquad S_{zz} \geq \tfrac{1}{3}LD_r^{max} \quad (5)$$

where LD_r^{min} and LD_r^{max} are the minimum and maximum values of the reduced dichroism, respectively, observed among all in-plane transitions (both ultraviolet and infrared) of a molecule in a polymer/solute system at a given stretch ratio.

For guanosine one knows the linear dichroism associated with two independent transitions, the amino-bending and the carbonyl-stretching vibrations whose transition moments may be taken to coincide with the C(2)–NH_2 and C(6)–O bonds in the guanine moieties. Using eq 4 for these two transitions defines the range of permissible values of the orientation factors shown by the thick line in Figure 8a. Here the value of S_{zz} was taken to be

$$0.17 \leq S_{zz} \leq 0.32$$

where the lower limit is based on the general inequalities (5) and the upper limit on the assumption that the correlation of z axis of guanosine with the stretch direction is not better than that of 9-aminoacridine.[25] The orientation angle that is obtained simultaneously is at an angle of $-52 \pm 2°$ from the C(2)–NH_2 bond direction as shown in Figure 9a.

In the case of 7-methylguanine, due to the overlap of neighboring bands, the dichroism of the amino band cannot be ascertained and experimentally only the value of the linear dichroism of the carbonyl stretch may be obtained. We now define the most likely region of orientation parameters as shown in Figure 8b by the general criteria represented by the inequalities (5) and the line that has been found to apply for guanosine and shown in Figure 8a. The orientation axis that one now calculates by means of eq 4 is at an angle of $\pm 76 \pm 9°$ from the C(6)–O bond direction.

For the silver complexes the only restrictions one is justified to use are those given by the inequalities (5), and the corresponding range of orientation factors are represented by the areas surrounded by thick solid lines in Figure 8, a and b, for guanosine–silver and 7-methylguanine–silver complexes respectively.

Discussion

Guanosine and Its Silver Complex. The resolution of the experimental solution spectrum of guanosine into two transitions above 230 nm shown in Figure 2a agrees well with π-electron

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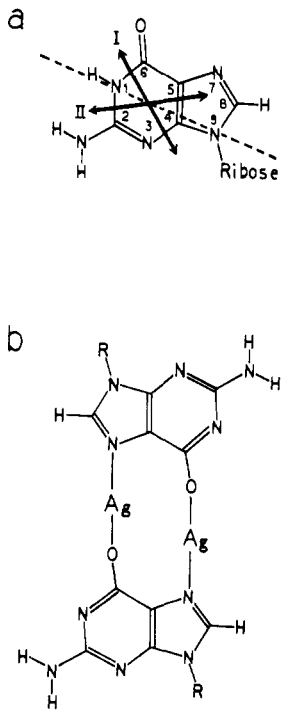

Figure 9. (a) Orientation axis (---) and transition moment directions of guanosine. (b) Proposed dimer structure of guanosine–silver complex.

SCFMO calculations. The positions and relative intensities of the π^*,π transitions in the relevant region are shown in Figure 2b; these have been calculated by the method and parametrization due to Bailey.[18] The geometry of the guanine moiety was taken to be that of guanosine dihydrate[26] for the purposes of the theoretical calculations.

In Figure 9a are shown the orientation axis of guanosine and the directions of the transition moments of the two in-plane π^*,π transitions relative to the molecular framework. The latter two were calculated by means of eq 4 with the observed UV dichroism shown in Figure 6a and the requirement that they should be similar to those found previously for guanine.[21] For the sake of comparison we give in Table III the estimated UV transition moment directions for guanine and for guanosine relative to the C(4)–C(5) bond direction.

Upon complexation with silver the ultraviolet spectrum may be decomposed into the vibronic progressions shown in Figure 2c. Relative to guanosine the transitions in the silver complex are shifted significantly in energy implying that the effect of the complexed silver ion is more than a relatively weak perturbation of the electronic levels of guanosine. This observation taken together with the simultaneous disappearance in the silver complex of the carbonyl-stretching vibrational mode (Figure 7, a and e) lends strong support to the suggestion[13] that silver binding occurs via the enolic tautomer of guanosine. As a further test of this model we calculated the theoretical positions and relative intensities of the π^*,π transitions of the enolic form of guanosine and these are shown in Figure 2d by the broken vertical lines. The full vertical lines correspond to the situation when a positive charge, representing a silver ion, is placed in the vicinity of the N(7) position as suggested by Tu et al.[13] These calculations were based on the method of Nishimoto et al.[27] modified slightly in view of some subsequent remarks made by the Baileys[28] which involves changing the core and γ parameters of the atom concerned and its immediate neighbors. These calculations may be seen to corroborate the model concerning the sites of silver attachment to the guanine moiety.

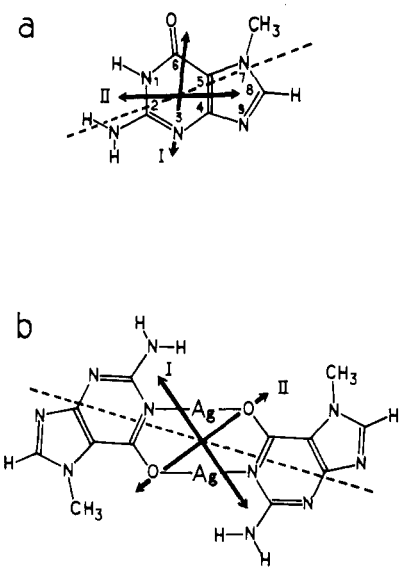

Figure 10. (a) Orientation axis (---) and transition moment directions of 7-methylguanine. (b) Proposed dimer structure of 7-methylguanine–silver complex and its orientation axis (---) and transition moment directions.

There is a very pronounced increase in the case of orientation of the silver complex relative to guanosine as may be seen from the results shown in Figure 8a suggesting that the complex is very likely of a dimeric form. The involvement of N(7) and the replacement of the enolic proton in guanosine on complexation leads then to a dimer model shown in Figure 9b; this model has previously been conjectured by Tu et al.[13] It is significant that the model shown is consistent with the large negative dichroism of the amino vibration in the complex seen in Figure 7e since one anticipates an orientation axis of the complex which is approximately perpendicular to the C(2)–NH_2 bond.

The $\Delta\epsilon$ values of the circular dichroism of the guanosine–silver complex are large; they suggest that the origin of this optical activity is exciton coupling between degenerate transitions and, in this way, lend further support to a model of the complex that is at least dimeric. If one makes the crude approximation that each degenerate coupling between transition moments occurs independently from the others one may use the parameters that describe the vibronic progressions in the absorption spectrum to calculate corresponding exciton CD spectra by the use of methods and procedures that have been described previously in detail.[29-31] Shown in Figure 3 are the results of such calculations where the exciton coupling was set arbitrarily to the relatively low strength of 300 cm^{-1} and the relative intensity of the two CD transitions was an adjustable parameter when fitting the experimental data. The fit generated by the solid lines for the first two transitions and by the broken line for the third, highest energy transition is good enough to accept the proposition that the observed spectrum has an exciton origin. This, in turn, implies that the coupled transition moments are not in a common plane; in the complex the bases are twisted relative to each other. Such a geometry is again consistent with the model that envisages the replacement of enolic protons by silver ions. We note that in view of the attachment of asymmetric D-ribose moieties to the bases one would not expect, in this case, that a racemic mixture of the twisted dimer conformation is found on complexation. As a result of the twisted conformation a quantitative evaluation of the linear dichroism data for the guanosine–silver complex could not be undertaken since the requirement of coplanarity of the orientation axis and the transition moments is violated.

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TABLE III: Estimates of the Transition Moment Directions[a,b]

	orientation/deg	
	transition I	transition II
guanine[c]	4 ± 3	−88 ± 4
guanosine	31 ± 9	−80 ± 11
7-methylguanine	−7 ± 14	−88 ± 22
7-methylguanine-Ag	9 ± 12	−79 ± 12

[a] Angles are measured relative to the C(4)-C(5) bond toward the C(6) atom. [b] Transitions are numbered in increasing energy. [c] Values from ref 21.

7-Methylguanine and Its Silver Complex. The resolution of the experimental solution spectrum of 7-methylguanine into two transitions shown in Figure 5a agrees with the results of theoretical calculations shown in Figure 5b. We take the orientation axis in the direction shown in Figure 10a, at an angle of −76 ± 9° from the carbonyl bond direction, as being the physically more acceptable alternative. Application of eq 4 to the ultraviolet dichroism results within the most likely range of orientation factors gives the values $|\theta_I| = 62 \pm 4°$ for the lowest energy, and $|\theta_{II}| = 19 \pm 13°$ for the next transition moment angle relative to the orientation axis. Of these we select, on analogy with guanine, the pair such that the lowest energy transition is nearly parallel to the C(4)–C(5) bond and almost perpendicular to the moment of the neighboring transition. These are shown in Figure 10a and in Table III.

Compared with 7-methylpurine the ultraviolet spectrum of the silver complex is red shifted with some changes also occurring in the relative intensities of the transitions. Basically, however, the spectrum of the complex may be regarded as that of the parent molecule perturbed by the attachment of the silver.

The disappearance of the carbonyl-stretching vibration on complexation (Figure 7f) provides strong evidence that the carbonyl group is involved in the reaction. At the same time the liberation of protons on complexation implicates the N(1) position as the point of attachment of the silver ions. Both these conditions would be met by a dimeric model of a 1:1 molar ratio complex between 7-methylguanine and silver ions based on the crystal structure of the silver–1-methylcytosine complex[32] and shown in Figure 10b. The formation of a dimeric species is consistent with the results shown in Figure 8b which show that the complex is more easily oriented than 7-methylguanine itself. Moreover, according to the models the 7-methylguanine dimer is less "rodlike" than the dimer of the guanosine–silver complex which would explain why the orientation of the latter is so much more pronounced (Figure 8a).

More quantitative calculations using the dichroism data are possible provided some assumption is made with respect to the values of the orientation factors of the 7-methylguanine–silver complex. We shall estimate their likely range to be

$$0.33 \leq S_{zz} \leq 0.42 \qquad -0.12 \leq S_{yy} \leq -0.06$$

Adopting these values we calculate from the dichroism of the amino-bending vibrational band that the orientation axis is at |74 ± 10°| relative to the C(2)–NH_i bond. We chose the positive value of this angle since, as shown in Figure 10b, this fits in well with a z-axis direction anticipated for the dimer model. Similarly, from the ultraviolet dichroism we estimate the angles between the transition moments and the orientation axis to be $|\theta_I| = 39 \pm 5°$ and $|\theta_{II}| = 53 \pm 5°$, respectively, for the lowest and next higher energy transitions. From a comparison of the resolved solution absorption spectra we have already concluded that the electronic structure of 7-methylguanine is not severely perturbed by the complexed silver ion. On this basis we select the pair of transition moments as shown in Figure 10b and in Table III. It may be seen from Table III that the correlation between the transition moment angles estimated for the two largest energy π^*,π transitions in guanine, 7-methylguanine, and the silver complex of 7-methylguanine is very satisfactory.

Conclusion

Both guanosine and 7-methylguanine form dimeric complex species with silver ions in neutral aqueous solution but with different structures. The structure of the guanosine–silver complex is most likely to involve the replacement of the enolic proton by silver and the simultaneous complexing to the N(7) nitrogen of a second guanosine molecule. The silver ion in the 7-methylguanine complex displaces the N(1) proton most probably and is complexed to the keto group of the second 7-methylguanine molecule. The results obtained should be of considerable help toward elucidating the structural changes brought about by silver ions in nucleic acids and polynucleotides.

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Oxidation Processes on CdSe and Se Electrodes

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Measurements of hole capture by various aldehydes, organic acids, and alcohols were performed on CdSe and Se-coated CdSe. It was found that CH_2O and $(CHO)_2$ are oxidized by reacting with photoproduced holes from the valence band of n-type CdSe and then reinjecting electrons into the conduction band (a process known as current doubling). This, however, only occurred in basic solution, and none of the other species tested showed this reaction. It was also found that the photodecomposition of CdSe in neutral solution proceeds as a current-multiplying reaction. These processes occurred just as readily with the Se layer, and it is concluded that the layer is porous. Mechanisms for these reactions are discussed.

Introduction

We have studied CdSe, a popular material for photoelectrochemical solar cells, as a possible selective photoanode to oxidize various organic species. An anodically biased CdSe electrode will supply holes under illumination to oxidize organic compounds of compatible redox potential with the valence band. At the cathodic electrode (e.g. platinum) the same compound may be reduced or the oxidized form may revert back. The former results in a disproportionation of the compound. For the case of aldehydes, disproportionation leads to an acid at the anode and an alcohol at the cathode.

The work of Gomes' group[1] on oxidation of organics by holes

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