negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC40539K.

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Heavy Metal–Nucleotide Reactions. IV. Nature of the Reaction between Mercury(II) and Uridine or Thymidine. Vibrational Spectroscopic Studies on Binding to N(3), C(4)=O, and C(5) of the Uracil Base[1]

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Mercurials can react with uracil, uridine, or thymidine in three different ways: coordination to a carbonyl oxygen of the neutral ligand, electrophilic attack on the ring with displacement of a proton and formation of a mercury–carbon bond, and electrophilic attack with displacement of a proton and formation of a mercury–nitrogen bond. Raman and, in part, infrared spectra have been obtained for model compounds representative of the first two types of binding. The spectra for both of these types of binding are very different from those observed previously for reaction of CH_3Hg^{II} with Urd in dilute aqueous solution at pH 8, where the spectra suggested the third type of binding reaction occurred. It is concluded that the only important reaction in dilute aqueous solution involves electrophilic attack at N(3) with substitution of the proton by mercury. Changes in the spectra are discussed in terms of LCAO–SCF calculations for the base and the base from which a proton has been lost.

Introduction

It has been assumed generally that in the pH range 7–9 reaction of mercury(II) or alkylmercury(II) ions with native DNA occurs first at the thymidine base with substitution of the proton on N(3) by Hg^{2+} or RHg^+.[2-12] The proton which is displaced normally is involved in hydrogen bonding to adenosine in the double helix. Of interest is how mercury(II) is able to interact with such a well-protected site at room temperature. In the case of alkylmercury(II) species, *e.g.*, CH_3Hg^+, it has been observed that there is a cooperative transition to denatured DNA which occurs above a critical concentration of the alkylmercury(II).[11] The characteristics of this reaction have been summarized recently by Beerman and Lebowitz,[12] who employed CH_3Hg^{II} to probe for unpaired bases in superhelical DNA.

Mercuric chloride reacts with uracil and dihydrouracil to yield crystalline 1:2 complexes in which the mercury(II) is six-coordinate with four bridging chlorides and two trans oxygens.[13] Only the C(4)=O oxygens are coordinated to mercury, while the C(2)=O oxygens are involved in intermolecular hydrogen bonding between Ura or h_2Ura molecules. The relatively short Hg–O interaction, 2.71 ± 0.02 Å for $HgCl_2 \cdot 2Ura$, together with the distortion of the oxygen out of the least-squares plane of Ura, suggests a rather strong Hg–O bond. If mercury(II) coordinates to the carbonyl oxygen rather than to the ring nitrogen of thymine in DNA, the ready reaction of mercurials with DNA without thermal activation could be explained by attack on the partially exposed C(4)=O oxygen in the large groove of the double helix. This has been discussed by Carrabine and Sundaralingam.[13]

Recently we have observed, using Raman difference spectrophotometry, changes in the spectra of Ura, Urd, and poly(U) upon reaction with CH_3Hg^{II} which indicated that the proton bound to N(3) was displaced, and mercury appeared to be bound to N(3). These studies were made with solutions at pH 8.[14] Carrabine and Sundaralingam crystallized the

$HgCl_2 \cdot 2Ura$ from a solution at pH 4.2, and they suggested that it was possible that deprotonation occurred at higher pH and that a different complex might be formed. In order to determine the effect of coordination of mercury(II) to the carbonyl oxygen on the vibrations of Ura, we have obtained Raman and infrared spectra of $HgCl_2 \cdot 2Ura$ in this work.

In all previous work, it has been assumed that the reactions of mercurials with Ura, Urd, and Thd occur at the same kind of site. Most experimental work has been carried out with Ura or Urd. We have found that CH_3Hg^{II} is a very strong electrophile in its reactions with pyrimidine[14] and purine[15] nucleosides and nucleotides. Recently Dale, Livingston, and Ward have observed another type of reaction with Urd-5'-PPP under relatively mild conditions.[16] Reaction of mercury(II) acetate with Urd-5'-PPP at 50° for 3 hr yields a product in which the ring is mercuriated at C(5); *i.e.*, the product is 5-mercuriuridine 5'-triphosphate. Since a number of studies on heavy metal–nucleotide reactions, particularly those dealing with the antitumor activity of certain platinum complexes,[17] have involved incubation of the solutions at 37° for rather long periods of time, we have examined the Raman spectra of 5-HgUTP to obtain marker frequencies for Urd metalated at the C(5) position.

From this work, fingerprint spectra are now available for Urd mercuriated at N3, C(4)=O, and C(5), and these can be used to ascertain the binding sites of other heavy metals to Urd in aqueous solution.

Experimental Section

$HgCl_2 \cdot Ura$. This compound was synthesized using the procedure described by Carrabine and Sundaralingam[13] by heating a solution 12.5 m*M* in $HgCl_2$ (Mallinckrodt, AR) and 25 m*M* in Ura (Sigma Chemical, St. Louis, Mo.) for 5 min and allowing the solvent to evaporate slowly at room temperature. *Anal.* Calcd for $C_8H_8N_4O_4Cl_2Hg$: C, 19.4; H, 1.63; Hg, 40.5. Found: C, 19.4; H, 1.71; Hg, 40.7. For Raman spectra, crystalline samples were sealed in capillary tubes.

5-Mercuriuridine 5'-Triphosphate. This compound was obtained from Terra-Marine Bioresearch, La Jolla, Calif., and was synthesized by the procedure of Dale, *et al.*[16] For the Raman spectra the compound was dissolved in doubly distilled water, the solution was made 0.1 *M* in $NaClO_4$ as an internal intensity and frequency reference, and the pH was adjusted to 7.

Raman Spectra. Spectra of the crystalline samples were obtained with both a Jarrell-Ash 25-300 instrument using a Spectra-Physics 125 He–Ne laser and an instrument built around a Spex 1400 double monochromator using a Spectra-Physics 112 He–Ne laser.[18] The former instrument gives particularly good quality spectra at small shifts, since the gratings are relatively ghost free. The latter instrument gives better spectra at large shifts (cooled RCA 31034A photomultiplier), and because it involves stepwise, digital data collection, it permits more thorough treatment of the data. Neon plasma lines are used for frequency calibration.

Raman difference spectra were excited with the 5145-Å line of a Coherent Radiation Model 52 Ar^+ laser operating at *ca.* 600 mW. The Spex 1400 monochromator–RCA 31034A system was used together with a programmed sample carrier for alternate positioning of sample and reference in the laser beam. Spectral analyses were carried out off-line on this university's CDC-6500 computer using PROGRAM RAMAN. The general procedure has been described previously,[14] and a detailed description of the spectrophotometer has been given elsewhere.[19]

Infrared Spectra. A Beckman IR-12 spectrometer calibrated *vs.* indene and polystyrene was used. Spectra were obtained with Nujol and halocarbon mulls. Polyethylene windows were employed to 650 cm^{-1}; NaCl plates, at higher frequency. To avoid the possibility of halide exchange between $HgCl_2 \cdot 2Ura$ and the mull plates, CsI windows were not used.

Data and Results

$HgCl_2 \cdot 2Ura$. The Raman and infrared spectra of microcrystalline $HgCl_2 \cdot 2Ura$ are illustrated in Figures 1 and 2 with the spectra of crystalline Ura for comparison. The frequencies, which show some differences between Ura and $HgCl_2 \cdot 2Ura$, are collected in Table I.

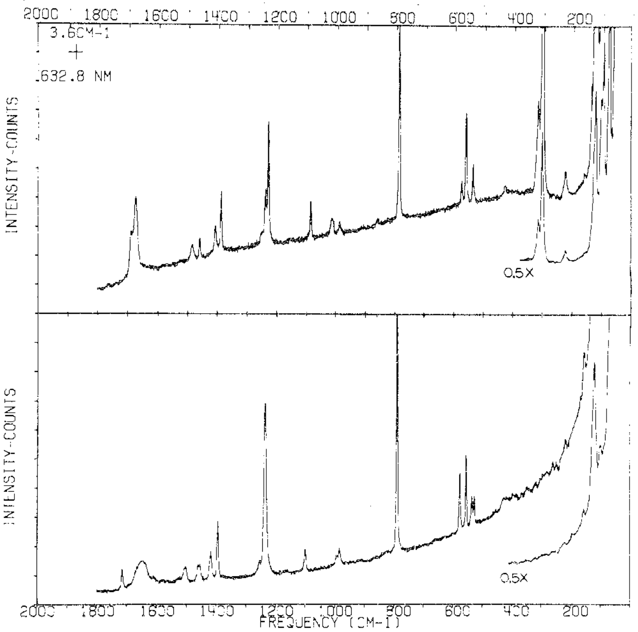


Figure 1. Raman spectra: top, microcrystalline $HgCl_2 \cdot 2Ura$; bottom, microcrystalline Ura. $\lambda_0 = 632.8$ nm; slits *ca.* 3.6 cm^{-1}.

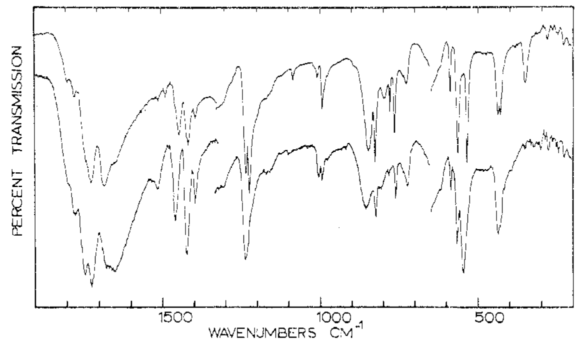


Figure 2. Infrared spectra, halocarbon and Nujol mulls: top, $HgCl_2 \cdot 2Ura$; bottom, Ura.

Table I. Raman and Infrared Frequencies (cm^{-1}) Characteristic of the Reaction of the Ura C(4)=O with $HgCl_2$

$\nu(HgCl_2 \cdot 2Ura)$		ν(Ura)		
Raman	Ir	Raman	Ir	Assignment
	1741 w, sh		1741 s	$\nu(C(2)=0)$, $\nu(C(4)=0)$, $\nu(C{=}C)$
	1722 s	1716 *0*	1720 s	
1689 *2*				
1672 *3*	1678 s		1675 s	
	1643 w, sh	1651 *4*, b	1645 s	
		1258 *0*, sh		
1238 *2*	1234 s	1238 *5*	1235 s	Single-bond str
1229 *4*	1222 s		1217 w, sh	
576 *1*		580 *2*		
560 *3*	562 s	559 *2*	566 m	δ ring
536 *1*	534 s	538 *0*	544 s, b	
		530 *0*	530 w, sh	
	349 m			$\nu_{as}(HgCl_2)$
316 *3*				$\nu_s(HgCl_2)$
302 *10*				

The Raman spectrum of crystalline Ura has been reported previously by Lord and Thomas[20] and the Raman and infrared spectra have been reported by Susi and Ard.[21] The Raman spectrum recorded in this work is very similar to that reported by Susi and Ard using 4880-Å excitation, and the frequencies compare favorably with those reported by Lord and Thomas.

The infrared frequencies agree closely with the values given by Susi and Ard.[21] Only relatively minor changes occur in the Ura modes upon binding to $HgCl_2$. The most striking change in the Raman spectrum is the large increase in the intensity of the scattering in the double-bond region, 1800–1500 cm^{-1}. Ura itself exhibits a very broad band centered at *ca.* 1650 cm^{-1} plus a weak band at *ca.* 1610 cm^{-1} and a more intense one at 1716 cm^{-1}. The $HgCl_2 \cdot 2Ura$ exhibits two intense bands at 1672 and 1689 cm^{-1}. At lower frequency, the broad Ura band at 1238 cm^{-1} splits into two very narrow bands at 1229, 1238 cm^{-1}. Rather similar effects are observed in the infrared spectra.

Although Susi and Ard carried out a normal-coordinate analysis for Ura, the exact nature of the normal modes is still uncertain. In the double-bond region are expected $\nu(C(2){=}O)$, in-phase $\nu(C(4){=}O) + \nu(C{=}C)$, and out-of-phase $\nu(C(4){=}O) + \nu(C{=}C)$. The extent of coordinate mixing is uncertain. In addition, the in-plane N–H deformation probably mixes with the C=O motion, since the spectrum of the N-deuterated derivative is somewhat different. Lord and Thomas[20] assumed mixing was significant; Susi and Ard[21] assumed it was not.

Ura crystallizes in the space group C_{2h}^5 ($P2_1/c$) with four molecules in the crystallographic and Bravais cell. The molecules are arranged in hydrogen-bonded dimers situated on C_i sites. There are N(3)–H···O(4) pairs and single N(1)–H···O(4) hydrogen bonds. The other carbonyl oxygen, O(2), is not involved in hydrogen bonding. As a consequence, the a' and a'' in-plane Ura modes (species for isolated molecule) couple to give A_g, A_u, B_g, and B_u crystal modes. Since the crystal is centric, Raman and infrared modes are not expected to be coincident.

The complex $HgCl_2 \cdot 2Ura$ crystallizes in the space group C_i^1 ($P\bar{1}$) with 1 formula unit per cell.[13] The mercury atom is on a center of symmetry; and the Ura molecules, situated on a general site, are hydrogen bonded in ribbons by N(3)–H···O(2) and N(1)–H···O(2) interactions. The mercury-bound C(4)=O is not involved in hydrogen bonding. In this crystal a' and a'' Ura modes (isolated molecule) of the two molecules each couple to give A_g and A_u crystal modes. Since the crystal is again centric, Raman and infrared bands are not expected to be coincident.

The sharpening of the bands above 1200 cm^{-1} in the spectrum of $HgCl_2 \cdot 2Ura$ compared with that of Ura is consistent with the reduction in the number of molecules in the unit cell. The general increase in the frequency of the Raman and infrared bands in the double-bond region 1600–1700 cm^{-1} is expected because of the coordination of the C(4)=O to mercury.

Since the $HgCl_2 \cdot 2Ura$ structure contains recognizable $HgCl_2$ molecules, the vibrations associated primarily with $HgCl_2$ would be expected to resemble those of $HgCl_2$ itself. For $HgCl_2 \cdot 2Ura$, $\nu_s(HgCl_2)$ correlates with an A_g crystal mode, while ν_{as} correlates with an A_u mode. The bending mode correlates with two A_u modes. Intense Raman scattering is observed at 300 cm^{-1} with a shoulder at 315 cm^{-1}. Only one Hg–Cl stretching band is expected, and this is taken as the intense band at 300 cm^{-1}. The separation between the main band and the shoulder would appear to be too large for isotopic splitting, and the intensities are not in the proper ratio. The relative intensities should be as follows: $Hg^{35}Cl_2$, 9; $Hg^{35}Cl^{37}Cl$, 6; $Hg^{37}Cl_2$, 1. In addition, a new Raman band occurs at 93 cm^{-1} with a shoulder at 100 cm^{-1}. A single infrared band at 349 cm^{-1} clearly is $\nu_{as}(HgCl_2)$. Mercury–oxygen stretching also should occur somewhere in this region, but its position is uncertain.

These values for Hg–Cl stretching can be compared with those of $HgCl_2$ which crystallizes in the space group D_{2h}^{16} (*Pnma*), with 4 molecules in the crystallographic and Bravais cell. The $\nu_s(HgCl_2)$ molecular modes give rise to A_g, B_{3g}, B_{1u}, and B_{2u} crystal modes as do the $\nu_{as}(HgCl_2)$ modes. Spectra of $HgCl_2$ have been discussed by Poulet and Mathieu[22] and by Mikawa, Jakobsen, and Brasch.[23] The Raman spectrum of $HgCl_2$ exhibits a very weak band at 375 cm^{-1}, $\nu_{as}(HgCl_2)$, symmetry species A_g, B_{3g}, and bands at 316, 310 cm^{-1}, $\nu_s(HgCl_2)$, A_g, B_{3g}. The infrared spectrum exhibits a very strong band at 368 cm^{-1} and weaker bands at 330, 310 cm^{-1}. The similarity in the frequency of the scattering derived from $HgCl_2$ stretching with that for $HgCl_2 \cdot 2Ura$ and $HgCl_2$ indicates that the bonding is similar in both systems. The bond distances also are similar. For $HgCl_2$, they are 2.25, 3.34, and 3.63 Å. Six chlorines are coordinated with pairs of equivalent bonds related by the center of symmetry. For $HgCl_2 \cdot 2Ura$, there are two kinds of Hg–Cl bonds, 2.30 and 3.07 Å. Again these occur in pairs related by the center of symmetry. The Raman- and infrared-active $HgCl_2$ stretching modes are *ca.* 10 and 20 cm^{-1} lower in $HgCl_2 \cdot 2Ura$, consistent with the presence of the short Hg–O bond, 2.71 ± 0.02 Å, found by Carrabine and Sundaralingam.[13]

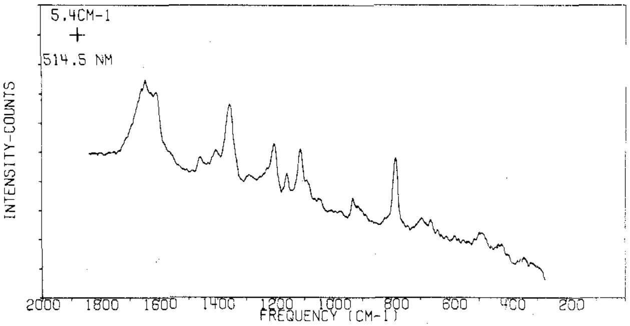


Figure 3. Raman difference spectrum: 18 m*M* 5-HgUTP and 100 m*M* ClO_4^- *vs.* 100 m*M* $NaClO_4$. $\lambda_0 = 514.5$ nm, slits *ca.* 5.4 cm^{-1}, 0.5-Å steps, and 10-sec count time. Solvent + perchlorate modes are canceled.

Table II. Ligand Raman Frequencies (cm^{-1}) for 5-HgUTP $CH_3HgUrdH_{-1}$, and Urd in Aqueous Solution

ν(Urd)	$\nu(CH_3HgUrdH_{-1})$	ν(5-HgUTP)
1676 *7*		1648 *10*
1630 *3*	1637 *8*	1612 *4*
1475 *1*		
	1458 *1*	1459 *2*
1425 *1*, sh		
1395 *3*	1386 *3*	1404 *3*
		1358 *9*
	1291 *3*	1292 *1*
1229 *10*	1236 *5*	
		1206 *6*
	1208[a] *4*	1161 *2*
991 *0*	1044	1115[b] *5*
861 *1*	862 *1*, b	
780 *4*	791 *3*	787 *8*
552 *1*	561[a] *10*	
		494 *2*
419 *0*		

[a] Internal modes of CH_3Hg^{II}. [b] Triphosphate mode.

5-Mercuriuridine 5'-Triphosphate. It proved to be impossible to obtain Raman spectra with the solid compound. It is isolated by lyophilization from ammonium bicarbonate column eluates and obtained as a white fluffy powder. This gave very effective diffuse reflectance of the laser beam, masking the Raman scattering.

An aqueous solution was prepared which was saturated in 5-HgUTP at pH 8. Using the values ϵ_{max}, λ_{max} = 10,100 M^{-1} cm^{-1}, 267 nm, the concentration was found to be 18 m*M*. The solution was 0.1 *M* in ClO_4^- as an internal intensity and frequency standard. A Raman difference spectrum was obtained *vs.* the solvent, 0.1 *M* $NaClO_4$. This is illustrated in Figure 3. The spectrum is very different from that of either Urd or $CH_3HgUrdH_{-1}$. Frequency and intensity values are collected in Table II, and data are given for Urd and $CH_3HgUrdH_{-1}$ for comparison.

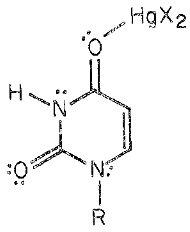
Since the solution was quite dilute, there was some uncertainty concerning the quality of the difference spectrum. As evidence for the reliability of the data, the symmetric mode involving PO_2 stretching may be considered. Rimai, *et al.*, made careful measurements of the Raman spectrum of 0.5 *M* Ado-5'-PPP at pH 7.5.[24] The triphosphate gives a sharp, intense band at 1112 cm^{-1}, and this is characteristic of triphosphates in general. In the difference spectrum, Figure 3, the corresponding band is clearly seen at 1115 cm^{-1}.

The frequencies characteristic of the Ura ring in Ura, Urd, and Urd-5'-P have been summarized by Lord and Thomas.[20] The following frequencies occur through a range of *ca.* ±10 cm^{-1} for all three species; the frequencies and relative intensities are those for Urd-5'-P: 786 *3*, 1233 *10*, 1391 *4*, b. Only the ring mode at 786 cm^{-1} is unaffected by mercuriation in the 5 position. All of the bands in the single- and double-bond stretching regions are markedly affected; particularly noteworthy is the disappearance of the most intense Urd mode at *ca.* 1233 cm^{-1}.

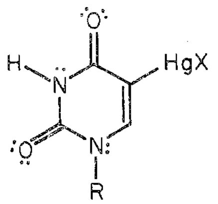
The envelope containing the bands arising from ν(C(2)=O), ν(C(4)=O), and ν(C(5)=C(6)) decreases by *ca.* 30 cm^{-1} compared to that for Urd-5'-P. This is to be expected, since substitution of the hydrogen on C(5) by mercury should markedly affect modes involving (C=C) stretching. This is strongly mixed with (C=O) stretching in at least two of the three normal coordinates responsible for scattering in this region.

Discussion

Three types of products appear to be obtainable by reaction of mercury(II) compounds with Urd or Ura. These are characterized by structures I–III. Structure I is observed for the crystalline product obtained by reaction of Ura and $HgCl_2$ in aqueous solution at room temperature, pH 4.2.[13] Structure II occurs for the product of the reaction of Urd-5'-PPP and mercuric acetate in aqueous solution at 50°, pH 5. It has been shown that mercuriation occurs at C(5) by pmr, observation of stoichiometric loss of ^3H from the C(5) tritiated derivative, and iodination to the C(5) iodo derivative.[25] Although mercuriation at N(3) also would be expected, the reverse reaction is rapid. The crude product is purified by chromatography on a cellulose column using triethylammonium bicarbonate, pH 7.5, as an eluent. Nitrogen-bound mercury is removed from the nucleotide as the triethylamine complex. Structure III has been suggested for the product of the reaction of Urd (or Thd) with mercury(II) or methylmercury(II) at pH 7–9 in aqueous solution.



I



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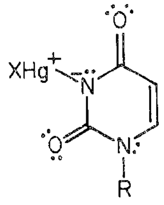
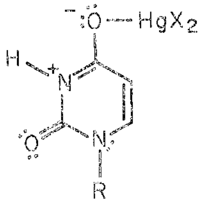


III

The crystal structure of $HgCl_2\cdot 2Ura$ shows that the bond distances in the Ura portion are all essentially the same in Ura itself and in the complex. In particular the C(4)=O bond length is 1.25 (3) Å in $HgCl_2\cdot 2Ura$ and 1.245 (2) Å for Ura. Consequently, there is no evidence for a shift to the electronic configuration IV under the influence of mercury(II). On this basis, one would expect the vibrations of Ura in $HgCl_2\cdot 2Ura$ to be very similar to those of Ura with an increase in the frequency of stretching modes involving the C(4)=O group. The expectation of an increase in the C(4)=O stretching frequency is based on the idea that replacement of a hydrogen bond by a bond to mercury will constrain further any motion of the oxygen atom. The infrared and Raman spectra of $HgCl_2\cdot 2Ura$ are essentially as predicted.



IV

In previous studies on the reaction of CH_3Hg^{II} with Urd at pH 8,[14] we suggested binding to N(3) with displacement of the proton, III. The pyrimidine and purine nucleosides in general have few good group frequencies. The most useful are the modes from *ca.* 1600 to 1700 cm^{-1} which involve C(2)=O, C(4)=O, and C(5)=C(6) stretching. These usually are described as carbonyl modes, since all of the early vibrational studies on these bases were done with infrared spectroscopy, and carbonyl vibrations have very high ir intensity. On the other hand, their Raman intensity is rather low, and the most intense scattering would be expected to arise from in-phase C(4)=O + C(5)=C(6) stretching. The intense scattering in this region decreases in frequency and increases in intensity when a proton is displaced from Urd,[14] Guo,[15] or Ino,[26] where the effect is virtually the same as with Guo. These frequency changes are the opposite of those observed for $HgCl_2\cdot 2Ura$ where mercury is known to bind to the carbonyl oxygen.

All-electron all-integral LCAO-SCF calculations for Thy and for Thy from which a proton has been removed from N(3)[27] indicate that about 0.75 electron migrates from N(3) and is distributed over the molecule approximately equally through the σ and π systems. The changes with Ura and Urd should be very similar. About 0.25 electron moves onto each carbonyl group, and 0.1 electron moves onto the C(5)=C(6) double bond. Substitution of H(3) by CH_3Hg^+ in Urd occurs with a decrease in frequency of the scattering in the 1600–1700 cm^{-1} range and an increase in intensity. This is precisely what should happen for a mode involving C(4)=O + C(5)=C(6) coordinates if binding of CH_3Hg^+ at N(3) permits extensive electron delocalization into the ring system such as occurs when the proton is displaced by reaction, *e.g.*, with NaOH, at high pH. In addition, the intense Urd band at 1229 cm^{-1} is replaced by medium bands at 1236 and 1291 cm^{-1}, and all of the lower frequency modes generally increase in frequency. The SCF calculations indicate that there is an increase in overlap charge for the C(2)–N(3) and C(4)–N(3) bonds of 0.15 electron as a proton is removed, so all of the lower frequency ring modes should increase. All of these effects are very different from those observed for $HgCl_2\cdot 2Ura$ where mercury(II) coordinates to the C(4) carbonyl oxygen. Clearly this has almost no effect on the election distribution in the ring.

Since our studies on the reactions of CH_3Hg^{II} with nucleosides and nucleotides[13,14] have indicated that methylmercury is a rather strong electrophile, it also seemed possible that a slow reaction forming a mercury–carbon bond might occur when CH_3Hg^{II} reacts with Urd in perchlorate solution at pH 8. The spectrum of the 5-HgUTP is entirely different from the spectrum of the complex formed by reaction of Urd with CH_3HgOH at pH 8. As would be expected for mercuriation at a ring carbon atom, the most intense Raman band which is characteristic of the Ura ring in Ura, Urd, and Urd-5'-P at 1233 cm^{-1} completely disappears in the 5-HgUTP. In a neutral or alkaline aqueous solution with perchlorate ion as was the case in these experiments, it is likely that the second coordination site of mercury(II) is occupied by OH^-.[2] Substitution occurs rapidly at mercury(II), so this can be displaced rapidly by better ligands, *e.g.*, mercaptides, chloride, etc.

It may be concluded that the reaction at 25° between Urd and Hg(II) or CH_3Hg^{II} in aqueous perchlorate solution at pH 7–9 involves displacement of the proton from N(3) and coordination of mercury. The solution Raman spectra are not at all consistent either with coordination to a neutral carbonyl oxygen or with an electrophilic attack at carbon. At high hydrogen ion concentrations or in the presence of a good ligand for mercury, *e.g.*, chloride ion, substitution of the ring proton is blocked and weak binding to a carbonyl oxygen can occur. The CH_3Hg^{II} ion apparently is not a sufficiently strong electrophile to displace H(5) and form the mercuri nucleotide at pH 8.

Registry No. $HgCl_2{\cdot}2Ura$, 53293-38-2; 5-Hg-UTP, 53293-39-3.

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Electron Paramagnetic Resonance Investigation of Crystal Field, Nuclear Quadrupole, and Structural Properties of Two Manganese(II) Compounds

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The electron spin resonance spectra of *trans*-$[Mn(acac)_2(H_2O)_2]$ doped into a diamagnetic, isomorphous host are reported. The unit cell parameters of another diamagnetic lattice, $[Zn(C_5H_5NO)_6](ClO_4)_2$, are reported ($C_5H_5NO$ is pyridine *N*-oxide), and the electron spin resonance spectra of $[Mn(C_5H_5NO)_6](ClO_4)_2$ in this host are reported. The principal features of interest are the large zero-field splittings in both compounds and a rhombic term in the acetylacetonate compound. The crystal field parameters are $D = 702$ G and $E = 205$ G in the acetylacetonate and $D = 410$ G for the C_5H_5NO compound. Also reported is the observation of $\Delta m = \pm 1$ lines, which are split by a nuclear electric quadrupole term, Q'. The parameters g, A, and B are also reported.

Introduction

Among the paramagnetic salts of the iron group, those of Fe(III) and Mn(II) are of special interest, for these ions behave as nearly ideal paramagnets.[1] The ^6S ground state is well isolated from the excited (optical) states, which causes many salts to exhibit a simple Curie behavior to low temperatures and also to have electronic relaxation times long enough such that many compounds exhibit electron spin resonance absorption at ambient temperatures. As a result, the epr spectrum of manganese(II) in particular has been reported in many host compounds, most of them being either hydrates or simple ionic salts.[2] Only a few chelate compounds[3] have been investigated, and so we report here an epr investigation of the divalent manganese chelate *trans*-diaquobis(acetylacetonato)manganese(II), *trans*-$[Mn(acac)_2(H_2O)_2]$. Also chosen for study was a divalent manganese salt hexakis(pyridine *N*-oxide)manganese(II) perchlorate, $[Mn(C_5H_5NO)_6](ClO_4)_2$.

The spectra are analyzed in terms of a spin Hamiltonian and the necessary parameters obtained. Of special significance, the use of single crystals and the large deviations from cubic symmetry have permitted the investigation of the nuclear electric quadrupole contribution to the splitting of nuclear forbidden transitions; the quadrupole terms are of current concern in discussions of chemical bonding.[4]

Experimental Section

trans-$[Mn(acac)_2(H_2O)_2]$ and the diamagnetic host compound *trans*-$[Mg(acac)_2(H_2O)_2]$ were prepared in a similar fashion. A stoichiometric amount of acetylacetone in methanol was added to an aqueous solution of $MnCl_2{\cdot}4H_2O$ and the mixture was made basic with sodium acetate.[5] After heating, the mixture was placed in the refrigerator for several hours. The light yellow precipitate was filtered under nitrogen and dried in a desiccator. The Mg(II) compound is white and it may also be prepared by making the acetylacetone–$MgCl_2{\cdot}6H_2O$ mixture basic with ammonium hydroxide. The Mn(II) compound is light sensitive and decomposes on prolonged exposure to the air, so it was kept under nitrogen and in the dark.

Single crystals of 0.5% $Mg(Mn^{II})(acac)_2(H_2O)_2$ were grown from dimethylformamide solution. The doped compound was prepared by allowing the $MgCl_2{\cdot}6H_2O$ to react with acetylacetone in the presence of 0.5% $MnCl_2{\cdot}4H_2O$. The crystals were grown by evaporating DMF under nitrogen and in the dark.