for 4-NH$_2$py. In agreement with a previous result,[14] this would indicate that a rather small degree of delocalization may suffice to affect the electron transfer process.

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Registry No. Fe(CN)$_5$(4-NH$_2$py)$^{3-}$, 68378-75-6; Fe(CN)$_5$OH$_2$$^{3-}$, 18497-51-3; 4-NH$_2$py, 504-24-5; Fe(CN)$_6$$^{3-}$, 13408-62-3; Fe(CN)$_5$py^{3-}, 37475-75-5; I$_3$$^-$, 14900-04-0; 2-methylpyrazine, 109-08-0.

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Heavy-Metal–Nucleoside Interactions. 13. Synthesis and Spectroscopic Study of Organomercury Derivatives of Guanosine and Thymidine[1,2]

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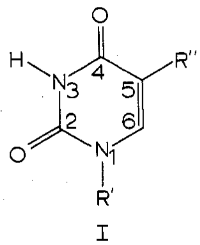
Complexes of the stoichiometry RHg(GuoH$_{-1}$), [RHg(Guo)]NO$_3$, and [(RHg)$_2$GuoH$_{-1}$]NO$_3$ have been synthesized by reaction of the nucleoside guanosine (Guo) and RHg^{II} in water (R = Me) or aqueous ethanol (R = Ph). Comparison of infrared spectra of the solid complexes and ^{1}H nuclear magnetic resonance spectra of the complexes in dimethyl-d_6 sulfoxide with spectra of Guo, [GuoH]NO$_3$, and Na[GuoH$_{-1}$]·H$_2$O allows assignment of structures for these ambidentate ligand complexes. Deprotonation of N$_1$ of Guo leads to coordination of RHg^{II} at N$_1$ in RHg(GuoH$_{-1}$) and to both N$_1$ and N$_7$ in [(RHg)$_2$GuoH$_{-1}$]NO$_3$. The complexes [RHg(Guo)]NO$_3$ have RHg^{II} bonded at N$_7$ of the guanine base. Phenylmercuric hydroxide reacts with thymidine (dThd) in aqueous ethanol to form PhHg(dThdH$_{-1}$)·H$_2$O with PhHg^{II} bonded to N$_3$ after deprotonation of dThd. Structures deduced for these solid complexes are in agreement with those suggested in earlier ultraviolet and Raman studies of the interaction of nucleosides and nucleotides with MeHg^{II} in aqueous solution. The uses and limitations of vibrational spectra in assigning structures to such metal nucleoside complexes are outlined.

The MeHg^{II} cation has been used for separations of polynucleotides with different base composition[4] and also as a simple unifunctional electrophile[5] to determine how spectroscopic properties of nucleotides alter with electrophilic attack at specific sites.[6–9] The spectroscopic perturbations are typical for heavy-metal binding and can be used to interpret data for other metal electrophiles.[2,10,11]

It has been observed that at low *r* values (total metal:total base), the first site of reaction with DNA's is N$_3$ of thymine and the second site N$_1$ of guanine bases.[9,12] The interaction with dThd[13] (I, R″ = Me, R‴ = H) and Urd (I, R″ = H, R‴ = OH) is well understood with both UV[14] and Raman[6a] spectral studies indicating binding to N$_3$ after deprotonation.

Guanosine (II, R‴ = OH) of the nucleosides exhibits the most complex reactions with MeHg^{II}. UV[14] and Raman studies[6b] on aqueous solutions of guanosine and GMP have indicated the formation of MeHg(GuoH$_{-1}$), [MeHgGuo]$^+$ and [(MeHg)$_2$GuoH$_{-1}$]$^+$ with binding at N$_1$, N$_7$, and both N$_1$ and N$_7$, respectively. Despite the extensive work with solutions, no solid complexes of MeHg^{II} have been isolated. In view of the importance of guanosine in the interaction of heavy metals with nucleotides, a series of MeHg^{II} and PhHg^{II} derivatives have been synthesized and characterized, together with a PhHg^{II} derivative of thymidine.



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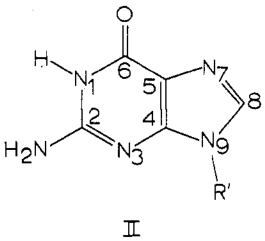

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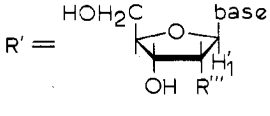

Experimental Section

Guanosine (Aldrich), thymidine (Sigma), and phenylmercuric hydroxide (Alfa) are commercially available and were used as received.

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Table I. Microanalytical Data for the Complexes[a]

complex	% calcd				% found			
	C	H	Hg	N	C	H	Hg	N
$MeHg(GuoH_{-1})$	26.5	3.0	40.3	14.1	26.3	3.3	40.0	14.3
$PhHg(GuoH_{-1})$	34.3	3.1	35.8	12.5	34.6	3.3	36.1	12.3
$[MeHg(Guo)]NO_3$	23.6	2.9	35.8	15.0	23.7	2.8	35.6	14.9
$[PhHg(Guo)]NO_3$	30.9	2.9	32.2	13.5	30.6	3.2	32.0	13.3
$[(MeHg)_2GuoH_{-1}]NO_3$	18.6	2.3	51.7	10.8	18.3	2.6	51.8	11.1
$[(PhHg)_2GuoH_{-1}]NO_3$	29.4	2.5	44.6	9.3	29.3	2.7	44.3	9.6
$[GuoH]NO_3$	34.7	4.1		24.3	34.4	4.3		24.0
$Na[GuoH_{-1}]\cdot H_2O$	37.2	4.4		21.7	37.2	4.4		21.9
$PhHg(dThdH_{-1})\cdot H_2O$	35.8	3.8	37.4	5.2	35.7	3.6	37.7	5.3

[a] Guo (guanosine) = $C_{10}H_{13}N_5O_5$; dThd (thymidine) = $C_{10}H_{14}N_2O_5$.

Methylmercuric nitrate was prepared by reaction of the iodide (in slight excess) with silver nitrate in water. The suspension was stirred for several days and filtered and the filtrate slowly evaporated to give crystalline methylmercuric nitrate.

Microanalyses were performed by the departmental microanalytical laboratory and are given in Table I. Infrared spectra (4000–400 cm^{-1}) of complexes in Nujol and halocarbon mulls were recorded with a Beckman Acculab 6 spectrophotometer, and ^{1}H NMR spectra at 60 MHz were measured with a Varian A-60A spectrometer.

Preparation of Complexes. Solvent removal during syntheses was accomplished by use of a rotary evaporator at ambient temperature, except for synthesis of MeHg^{II} complexes where the solvent was allowed to evaporate in a well-ventilated fume hood. All products were dried over phosphorus pentoxide at atmospheric pressure.

$MeHg(GuoH_{-1})$. Methylmercuric nitrate (1.509 g, 5.44 mmol) was added to a solution of guanosine (1.54 g, 5.44 mmol) in sodium hydroxide (0.19 M, 28.6 mL, 5.44 mmol). After the solution was stirred for 10 min and filtered to remove a small amount of undissolved guanosine, it was allowed to evaporate slowly. After 24 h a white solid was collected by filtration and washed with ethanol. The solid was stirred as a slurry in ethanol (30 mL) and water (3 mL) for 2 days, collected, and washed with ethanol (1.90 g, 70%). Infrared absorptions: 3325 (s, vb), 3210 (s, vb), 1625 (s), 1580 (m), 1527 (w), 1498 (m), 1413 (w), 1350 (m), 1312 (w), 1230 (w), 1204 (w), 1178 (w), 1124 (m), 1084 (m), 1050 (w, b), 1025 (m), 984 (w), 905 (w), 864 (w), 782 (w), 634 (w), 568 (w) cm^{-1}.

$PhHg(GuoH_{-1})$. A solution of guanosine (0.359 g, 1.27 mmol) and phenylmercuric hydroxide (0.387 g, 1.27 mmol) in ethanol (120 mL) and water (40 mL) was gently warmed and filtered, and 60 mL of solvent was removed. A small amount of precipitate (0.02 g) was removed by filtration, and after the solution was cooled at ca. −20 °C for 30 h a white precipitate was collected (0.435 g, 61%). Infrared absorptions: 3346 (s, b), 3210 (s, b), ca. 1660 (m, sh) and 1632 (s), 1579 (m), 1525 (m), 1508 (m), 1336 (m), 1306 (w), 1228 (w), 1183 (w), 1132 (m), 1090 (m), 1071 (w), 1047 (w), 1027 (m), 1000 (w), 986 (w), 914 (w), 868 (w), 780 (w), 738 (w), 703 (w), 642 (w), 574 (w), 460 (w) cm^{-1}.

$[MeHg(Guo)]NO_3$. A solution of methylmercuric nitrate (0.555 g, 2.00 mmol) in water (15 mL) was added to a stirred suspension of guanosine (0.567 g, 2.00 mmol) in water (50 mL). After 1 h a small amount of undissolved guanosine was collected, and the filtrate was evaporated to dryness to give a white solid. Ethanol (20 mL) was added, the suspension stirred for 7 h, and the white solid collected and washed with ethanol (0.756 g, 67%). Infrared absorptions: 3325 (s, b), 3200–3100 (s, vb), 1705 (s), 1641 (s), 1603 (s), 1541 (m), 1498 (m), 1388 (s, vb), 1218 (w, b), 1174 (m), 1117 (m), 1089 (m), 1050 (m), 1021 (w), 988 (w), 930 (w), 893 (w), 866 (w), 823 (w), 778 (w), 688 (w), 626 (w) cm^{-1}.

$[PhHg(Guo)]NO_3$. Nitric acid (0.204 M, 9.44 mL, 1.93 mmol) was added to a solution of phenylmercuric hydroxide (0.589 g, 1.93 mmol) and guanosine (0.545 g, 1.92 mmol) in ethanol (200 mL) and water (50 mL). On removal of ca. 200 mL of solvent a small amount of white precipitate (0.028 g) was removed by filtration. The filtrate was reduced to ca. 15 mL and cooled at ca. −20 °C for 2 h, and a white precipitate was collected in cooled glassware and washed with cooled ethanol (0.724 g, 60%). Infrared absorptions: 3330 (m, vb), 3220–3100 (m, vb), 1690 (s), 1638 (s), 1594 (s), 1538 (m), 1490 (m), ca. 1365 (s, vb), 1175 (m), 1080 (m, b), 1054 (m), 1019 (w), 994 (w), 908 (w), 860 (w), 821 (w), 795 (w), 774 (w), 729 (w), 694 (w), 621 (w), 452 (w) cm^{-1}.

$[(MeHg)_2GuoH_{-1}]NO_3$. A solution of methylmercuric nitrate (0.898 g, 3.23 mmol) in water (5 mL) was added to a solution of guanosine (0.448 g, 1.58 mmol) and sodium hydroxide (0.19 M, 8.33 mL, 1.58 mmol) in water (5 mL). After 2 days of slow evaporation a white solid was collected, washed quickly with water, and dried over phosphorus pentoxide (0.750 g, 61%). Infrared absorptions: 3325 (m, b), 3200 (m, b), 3125 (m, b), 1647 (s) and 1638 (s), 1600 (s), 1560 (w), 1525 (m, sh) and 1506 (s), ca. 1330 (s, vb), 1177 (w), 1115 (w), 1080 (m), 1035 (w), 996 (w), 914 (w), 889 (w), 869 (w), 823 (w), 800 (w), 776 (w), 736 (w) cm^{-1}.

$[(PhHg)_2GuoH_{-1}]NO_3$. Nitric acid (0.204 M, 6.06 mL, 1.24 mmol) was added to a solution of phenylmercuric hydroxide (0.757 g, 2.48 mmol) and guanosine (0.350 g, 1.24 mmol) in ethanol (290 mL) and water (30 mL). The solution was filtered and reduced in volume in ca. 50 mL, and after the solution was cooled at ca. −20 °C for 24 h, a white precipitate was collected and washed with ethanol (0.650 g, 58%). Infrared absorptions: 3325 (m, b), 3205 (m, b), 3125 (m, b), 1630 (s), 1601 (s), 1525 (m, sh) and 1500 (s), ca. 1330 (s, vb), 1180 (w), 1115 (w), 1083 (m), 1037 (w), 1022 (m), 997 (w), 915 (w), 890 (w), 865 (w), 825 (w), 783 (w), 695 (w), 624 (w), 453 (w) cm^{-1}.

$[GuoH]NO_3$. A solution of guanosine in 0.204 M nitric acid was immediately reduced to low volume by rotary evaporation at ambient temperature, and a white precipitate was collected and washed quickly with water. Infrared absorptions: 3325 (s, b), 3205 (s, b), 3120 (s, b), 1714 (s), 1650 (s), 1610 (s), 1544 (m), 1480 (w), 1370 (s, vb) and 1325 (s, vb), 1133 (m), 1086 (s), 875 (w), 827 (w), 778 (w), 693 (w), 675 (w), 615 (w) cm^{-1}.

$Na[GuoH_{-1}]\cdot H_2O$. A solution of guanosine (0.692 g, 2.44 mmol) in sodium hydroxide (0.19 M, 30 mL) was filtered and reduced to ca. 2 mL. The colorless oil obtained solidified to a white powder on stirring with ethanol for 2 h. The powder was collected, washed with ethanol, dried under vacuum, and dried over phosphorus pentoxide (0.585 g, 74%). Infrared absorptions: 3560 (m), 3495 (m), ca. 3260–3100 (s, vb), ca. 1674 (m, sh) and 1624 (s, sh) and 1595 (s, b), 1523 (m), 1482 (s), 1409 (s), 1344 (s) and 1331 (s), 1299 (m), 1227 (m), 1200 (m), 1139 (s) and 1126 (m), 1081 (s), 1051 (m), 1019 (w), 994 (w), 923 (m) and 913 (m), 874 (w), 807 (w), 640 (w) and 630 (w, sh), 567 (w) cm^{-1}.

$PhHg(dThdH_{-1})\cdot H_2O$. A solution of thymidine (0.400 g, 1.65 mmol) in water (20 mL) was added to a solution of phenylmercuric hydroxide (0.504 g, 1.65 mmol) in ethanol (150 mL). On removal of solvent a colorless oil was obtained, and this formed a fine white powder on stirring vigorously with water (20 mL). The powder was collected and purified by dissolving it in ethanol, filtering, and removing solvent to give an oil which solidified on stirring with water (0.5 g, 56%). Infrared absorptions: 3330 (s, vb), 3055 (w), 1646 (s), 1581 (s) and ca. 1542 (m, sh), 1435 (w, b), 1395 (w), 1288 (m), 1220 (vw), 1182 (w), 1140 (vw), 1091 (m) and 1071 (vw, sh), 1047 (m), 1017 (vw), 992 (vw) and 983 (vw) and 975 (vw), 912 (vw), 767 (w), 729 (m), 691 (w), 626 (w), 570 (vw), 500 (vw), 449 (w) cm^{-1}.

Results

Preparation of Complexes. Syntheses were designed to encourage formation of complexes with stoichiometries indicated from aqueous solution studies,[6b,14] and for all complexes simple metathesis reactions were successful. Methylmercury(II) complexes were prepared from $MeHgNO_3$ in water and, as suitable PhHg^{II} reagents are less soluble in water, the PhHg^{II} complexes were prepared from PhHgOH in aqueous ethanol.

The neutral complexes were prepared with reagents mixed in the stoichiometries indicated in eq 1–3. Preparation of

$$MeHgNO_3 + NaOH + Guo \rightarrow MeHg(GuoH_{-1}) + NaNO_3 + H_2O \quad (1)$$

$$PhHgOH + Guo \rightarrow PhHg(GuoH_{-1}) + H_2O \quad (2)$$

$$PhHgOH + dThd \rightarrow PhHg(dThdH_{-1})\cdot H_2O \quad (3)$$

$[RHg(Guo)]NO_3$ requires retention of protons by Guo and results from a simple addition reaction for MeHg^{II} (eq 4) but

$$MeHgNO_3 + Guo \rightarrow [MeHg(Guo)]NO_3 \quad (4)$$

for PhHg^{II} requires neutralization of PhHgOH (eq 5).

$$PhHgOH + HNO_3 + Guo \rightarrow [PhHg(Guo)]NO_3 + H_2O \quad (5)$$

Preparation of $[(RHg)_2GuoH_{-1}]NO_3$ requires deprotonation

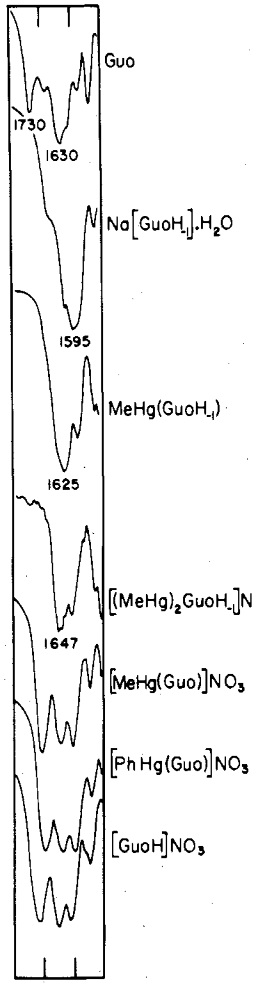


Figure 1. Infrared spectra of Guo, $Na[GuoH_{-1}]\cdot H_2O$, $MeHg(GuoH_{-1})$, $[(MeHg)_2GuoH_{-1}]NO_3$, $[MeHg(Guo)]NO_3$, $[PhHg(Guo)]NO_3$, and $[GuoH]NO_3$ as Nujol mulls in the region 1800–1500 cm^{-1}.

of Guo and 2 mol of RHg^{II}/1 mol of Guo, suggesting reactions 6 and 7 which were found to be successful.

$$2MeHgNO_3 + NaOH + Guo \rightarrow [(MeHg)_2GuoH_{-1}]NO_3 + NaNO_3 + H_2O \quad (6)$$

$$2PhHgOH + HNO_3 + Guo \rightarrow [(PhHg)_2GuoH_{-1}]NO_3 + 2H_2O \quad (7)$$

Salts containing $[GuoH]^+$ and $[GuoH_{-1}]^-$ were obtained from solutions of Guo in ca. 0.2 M HNO_3 and NaOH, respectively. The nitrate $[GuoH]NO_3$ must be isolated quickly to avoid decomposition, and the sodium salt $Na[GuoH_{-1}]\cdot H_2O$ is formed as an oil on slow evaporation of water but may be converted to a powder on stirring with ethanol.

Infrared Spectra. The nitrate complexes have strong, broad absorption in the region 1400–1300 cm^{-1} characteristic[15] of free or very weakly coordinated nitrate ion as found in crystallographic studies of organomercury(II) complexes containing this ion.[16] The sodium salt $Na[GuoH_{-1}]\cdot H_2O$ is formulated as a monohydrate on the basis of microanalysis (Table I), and presence of water is also indicated in its IR spectrum which has well-resolved antisymmetric and symmetric stretching frequencies for the water molecule at 3560 and 3495 cm^{-1} as part of broad $\nu(OH)$ (ribose) and $\nu(NH_2)$ absorption. Complexes of different stoichiometry, i.e., $RHg(GuoH_{-1})$, $[RHg(Guo)]NO_3$, and $[(RHg)_2GuoH_{-1}]NO_3$ have different IR spectra and for $MeHg^{II}$ and $PhHg^{II}$ complexes of the same stoichiometry spectra are very similar throughout the range measured. In Figure 1 spectra of the $MeHg^{II}$ complexes, Guo, Guo salts, and $[PhHg(Guo)]NO_3$ in the range 1800–1500 cm^{-1} illustrate these points.

Assignment of structures for the complexes by comparison of IR spectra requires caution, as Tsuboi et al.[17] have shown that Guo occurs in at least two crystalline forms. These forms have quite different spectra, particularly in the region 1800–1500 cm^{-1} where $\nu(C_6{=}O)$ and NH_2 deformation modes occur.[17] This arises presumably from differences in hydrogen bonding.

Solid guanosine has been reported to have IR absorptions at 1735 ($\nu(C_6{=}O)$) and 1635 cm^{-1} (NH_2 def)[18] (1730 and 1630 cm^{-1} (this work)). In Me_2SO solution the hydrogen bonding is weakened, and the corresponding absorptions are at 1692 and 1639 cm^{-1}.[19] In D_2O solution, $\nu(C_6{=}O)$ is observed at 1665 cm^{-1}, and deprotonation at N_1 shifts this below 1600 cm^{-1}.[19] Raman spectra of D_2O solutions locate $\nu(C_6{=}O)$ at 1670 cm^{-1}, while the corresponding band with H_2O is at 1680 cm^{-1}.[20] In both cases deprotonation shifts this below 1590 cm^{-1}. In the solid $Na[GuoH_{-1}]\cdot H_2O$, a broad IR band is observed centered at 1595 cm^{-1}, while a similar band has been reported for $K[GuoH_{-1}]$: 1630 (sh), 1587 (b, s) ν(ring), 1565 (b, s) cm^{-1}.[21] Since the marked shift with anionic guanosine to lower frequency of $\nu(C_6{=}O)$ is observed both with dilute aqueous solutions and in the crystalline guanosinates, it can be attributed only to deprotonation at N_1 and not to metal–oxygen interactions as sometimes has been claimed.[22]

The complexes of stoichiometry $RHg(GuoH_{-1})$ and $[(RHg)_2GuoH_{-1}]NO_3$ (R = Me, Ph) have IR spectra similar to that of $Na[GuoH_{-1}]\cdot H_2O$ (Figure 1) exhibiting a marked decrease in $\nu(C_6{=}O)$ and thus indicating that they contain the $[GuoH_{-1}]^-$ moiety as a ligand with deprotonation at N_1. The IR spectra do not define the binding site.

In Raman spectra of aqueous solutions of dThd-5′-P, a band involving mainly carbonyl stretching is observed at 1663 cm^{-1} which shifts to 1581 cm^{-1} upon deprotonation at N_3.[9] This mode is observed at 1648 cm^{-1} on formation of a complex with $MeHg^{II}$.[9] IR absorptions of solid dThd in the double bond region at 1708 and 1660 cm^{-1} are lowered to 1646 and 1581 cm^{-1} on formation of $PhHg(dThdH_{-1})\cdot H_2O$. The exact nature of these modes is unknown, but in related uracil[23] and uridine[20] spectra IR absorptions in this region have been assigned as $\nu(C{=}O)$ for the higher frequency band and in-phase $\nu(C_4{=}O) + \nu(C_5{=}C_6)$ for the lower band.

Changes in IR[19] and Raman spectra[20] of Guo at pH <2 in aqueous solution are consistent with protonation at N_7, and a crystallographic study of guanine hydrochloride, $[GuaH]Cl\cdot 2H_2O$, indicates that this does occur for guanine.[24] Infrared spectra of Guo and $[GuoH]NO_3$ as solids are similar in the region 1800–1500 cm^{-1}, and spectra of $[RHg(Guo)]NO_3$ (R = Me, Ph) resemble those of $[GuoH]NO_3$ very closely (Figure 1). Close similarity of these spectra, particularly the small lowering of $\nu(C_6{=}O)$ from 1730 in Guo to 1714 cm^{-1} in $[GuoH]NO_3$ and to 1705 cm^{-1} (R = Me) and 1690 cm^{-1} (R = Ph) in $[RHg(Guo)]NO_3$, indicates retention of the proton at N_1 with the second proton or RHg^{II} bonded to Guo elsewhere, presumably at N_7.

^1H NMR Spectra and Structures of the Complexes. ^1H NMR spectra of the complexes were obtained for solutions in dimethyl-d_6 sulfoxide as the solid complexes are expected to retain their molecular structures on dissolution in this solvent. Data for protons of the bases, RHg^{II} moieties, and the ribose proton H_1' are given in Table II. Other ribose protons are only marginally affected on complex formation, and data for their resonances are available as supplementary material (Table III).

Analogous $MeHg^{II}$ and $PhHg^{II}$ complexes have very similar spectra for base protons and H_1', and integrated intensities

Table II. ^{1}H NMR Data for the Complexes[a,h]

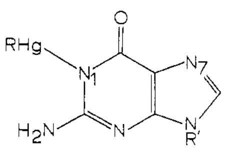
complex	N_1H	NH_2	H_8	H_1'	RHg^{II}	$\|^2J(^1H-^{199}Hg)\|$[b]
Guo	10.70	6.47	7.96	5.74 d[c]		
$[GuoH]NO_3$	*d*	*d*	9.17	5.87 d[c]		
$Na[GuoH_{-1}]\cdot H_2O$		7.0[e]	7.70	5.73 d[c]		
$MeHg(GuoH_{-1})$		6.38	7.85	5.72 d[c]	0.76	206.5
$PhHg(GuoH_{-1})$		6.53	7.88	5.74 d[c]	7.4 m	
$[MeHg(Guo)]NO_3$	11.45	7.02	8.69	5.90 d[c]	0.89	229
$[PhHg(Guo)]NO_3$	11.52	7.03	8.80	5.95 d[c]	7.42 m	
$[(MeHg)_2GuoH_{-1}]NO_3$		6.97	8.60	5.88 d[c]	0.85	221
$[(PhHg)_2GuoH_{-1}]NO_3$		*f*	8.74	5.96 d[c]	7.37 m	

complex	N_3H	Me	H_6	H_1'	RHg^{II}
dThd	11.18	1.80	7.71	6.20 t[g]	
$PhHg(dThdH_{-1})\cdot H_2O$		1.83	7.71	6.26 t[g]	7.4 m

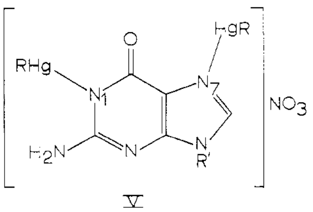
[a] In dimethyl-d_6 sulfoxide; chemical shifts (ppm) from internal tetramethylsilane. NMR data for the ribose group in the complexes are given in the supplementary material. [b] Coupling (Hz) to the methyl protons: the sign of the coupling constant is assumed to be negative.[25] [c] $J_{H_1', H_2'}$ = 5–6 Hz. [d] A resonance at 7.75 ppm is broad and integrates for 7 protons and thus includes NH_x and OH protons. [e] A resonance at 5.21 ppm (broad, 7 H) includes NH_2, OH, and H_2O protons. [f] Amine resonance within Ph multiplet (12 H). [g] $J_{H_1', H_2'}$ = 6.5 Hz. [h] d = doublet; t = triplet; m = multiplet.

confirm stoichiometries suggested from microanalyses. The spectra confirm deprotonation of N_1 of Guo in $RHg(GuoH_{-1})$ and $[(RHg)_2GuoH_{-1}]NO_3$, and of N_3 of dThd in $PhHg(dThdH_{-1})\cdot H_2O$ as suggested from IR spectra, and retention of the exocyclic NH_2 resonance in all complexes of Guo indicating that RHg^{II} moieties are not bound to this site. As suggested from IR spectra, the proton at N_1 of Guo is retained in $[RHg(Guo)]NO_3$ and is shifted downfield ca. 0.8 ppm on formation of the cationic complexes.

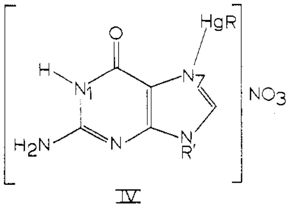
The nitrogen atoms N_1 and N_7 have pK_a values of 9.24 and 2.23, respectively,[26] and very weakly basic N_3 is generally considered not to be a site for complex formation with metal ions. Organomercury(II) moieties are expected to bind to the most basic donor, N_1, in forming $RHg(GuoH_{-1})$ (III), since good linear free energy relations are observed for protonation and methylmercuriation.[27] Both ^{1}H NMR and IR spectra are consistent with III, structures IV and V for $[RHg(Guo)]NO_3$ and $[(RHg)_2GuoH_{-1}]NO_3$, respectively, and structure VI for $PhHg(dThdH_{-1})\cdot H_2O$.



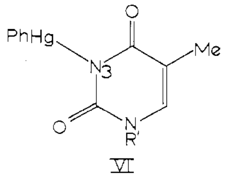
III



V



IV



VI

Table IV. Comparison of Raman Fingerprint Frequencies for Coordination of Electrophiles to Different Sites of Guo-5′-P with Infrared Absorptions Sensitive to Coordination in Solid Guo Complexes

	electrophile coordinated to		frequency, cm^{-1}		
complex	N_7	N_1	I	II	III
	Raman (H_2O)				
Guo-5′-P[a]		H^+	1680	1578	1490
MeHg(Guo-5′-P)[b]	$MeHg^{II}$	H^+	1677	1599	1496
GuoH-5′-P[c]	H^+	H^+	1710	1612	
$MeHg(GuoH_{-1}$-5′-P)[d]		$MeHg^{II}$		1600	1500, 1466
$GuoH_{-1}$-5′-P[e]				1590	1478
	Infrared (Nujol or Halocarbon Mulls)				
Guo, this work		H^+	1730	1573	1489, 1540
Guo, form I[f]		H^+	1730, 1692	1570	1480, 1540
Guo, form II[f]		H^+	1736	1573	1488, 1535
$[MeHg(Guo)]NO_3$	$MeHg^{II}$	H^+	1705	1603	1498, 1541
$[PhHg(Guo)]NO_3$	$PhHg^{II}$	H^+	1690	1594	1490, 1538
$[GuoH]NO_3$	H^+	H^+	1714	1610	1480, 1544
$MeHg(GuoH_{-1})$		$MeHg^{II}$	*g, h*	1580	1498, 1527
$PhHg(GuoH_{-1})$		$PhHg^{II}$	*g, h*	1579	1508, 1525
$[(MeHg)_2GuoH_{-1}]NO_3$	$MeHg^{II}$	$MeHg^{II}$	*g, h*	1600	1506, 1525
$[(PhHg)_2GuoH_{-1}]NO_3$	$PhHg^{II}$	$PhHg^{II}$	*g*	1601	1500, 1525
$Na[GuoH_{-1}]\cdot H_2O$			*h, i*	*h*	1482, 1523

[a] Reference 20; pH 7.5. [b] Reference 6b; pH 2. [c] Reference 20; pH 0.5. [d] Reference 6b; pH 8.5. [e] Reference 20. [f] Reference 17. [g] Part of broad absorption 1660–1600 cm^{-1}. [h] See Figure 1. [i] Part of broad absorption 1675–1560 cm^{-1}.

Further evidence for these structures comes from trends in H_8 and H_1' resonances and in the coupling constant ^2J (^{1}H–^{199}Hg) for the $MeHg^{II}$ moiety (Table II). Both H_8 and H_1' are deshielded on formation of $[GuoH]NO_3$, $[RHg(Guo)]NO_3$, and $[(RHg)_2GuoH_{-1}]NO_3$, consistent with binding of an electrophile at N_7. In a series of $MeHg^{II}$ complexes of pyridine and substituted pyridines, $[MeHgL]NO_3$, the coupling constant $^2J(^1H-^{199}Hg)$ increases with decreasing basicity (or pK_a) of the pyridine donor.[28] Consistent with structures III and IV, $MeHg(GuoH_{-1})$ has a coupling constant of 206.5 Hz, while $[MeHg(Guo)]NO_3$ has a coupling constant of 229 Hz as N_7 is less basic than N_1. The complex $[(MeHg)_2GuoH_{-1}]NO_3$ has a $^2J(^1H-^{199}Hg)$ of 221 Hz, intermediate between these two values, consistent with binding at both sites with rapid exchange of $MeHg^{II}$ between N_1 and N_7.

Discussion

The solid complexes isolated from water (R = Me) or aqueous ethanol (R = Ph) have been shown by IR and NMR spectroscopy to have structures III–VI as have previously been suggested for solution species by UV[14] and Raman[6b] studies of aqueous solutions of Guo and Guo-5′-P, respectively. The much larger coupling constants observed with oxygen donors[5] coupled with values of known stability constants of CH_3Hg^+ [e.g., for imidazolate log K_1 = 11.8, for imidazole 7.1, and for phenolate 5.5[27]] allow binding to the exocyclic oxygen to be ruled out. Mercury–proton spin–spin coupling constants have been used previously to identify the ligating atom in complexes of ambidentate ligands including amino acids,[5] but this is the first application to nucleic acid constituents.

From Raman studies, characteristic "fingerprint" frequencies for coordination of electrophiles at different sites of Guo-5′-P have been tabulated.[11] Results for H^+ and $MeHg^{II}$ as electrophiles are reproduced in Table IV and compared with IR spectra of solid complexes in the same region. The three Raman modes have been described[11] as $\nu(C_6{=}O)$ (I), $\nu(C_4{=}C_5) + \nu(C_5{-}C_6)$ in-phase (II), and a purine mode (III).

Although Raman and IR modes in the same region may be different in some cases, Table IV indicates that similar trends occur in both Raman and IR bands. Thus, bands II and III increase in frequency on replacement of the proton on N$_1$ by RHg^{II}, and band II increases in frequency on addition of an electrophile to N$_7$ when N$_1$ remains protonated. Band shifts most diagnostic of reaction are I and the IR absorption found at 1540 cm^{-1} in Guo. All species formed with deprotonation at N$_1$ show a marked decrease in the frequency of I, and the absorption at 1540 cm^{-1} is lowered to 1527–1523 cm^{-1}.

Comparison of the IR and Raman data in Table IV with each other and with those of Table II of ref 11, which includes species with N$_7$-bound metal, shows that vibrational spectra give a clear indication *only* of the state of protonation of N$_1$. They alone do not demonstrate whether metal binding is at N$_1$, N$_7$, or conceivably O$_6$.

Registry No. MeHg(GuoH$_{-1}$), 68630-40-0; PhHg(GuoH$_{-1}$), 68630-41-1; [MeHg(Guo)]NO$_3$, 68629-63-0; [PhHg(Guo)]NO$_3$, 68682-88-2; [(MeHg)$_2$GuoH$_{-1}$]NO$_3$, 68629-65-2; [(PhHg)$_2$GuoH$_{-1}$]NO$_3$, 68629-67-4; [GuoH]NO$_3$, 68630-42-2; Na[GuoH$_{-1}$], 61393-37-1; PhHg(dThdH$_{-1}$), 68630-43-3.

Supplementary Material Available: Table III, NMR data for the ribose group in the complexes (1 page). Ordering information is given on any current masthead page.

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Cationic Carbene Complexes of the (Pentachlorophenyl)nickel(II) Moiety and the Spectrochemical Series of Neutral Carbon Ligands

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A series of stable cationic complexes *trans*-[C$_6$Cl$_5$Ni(PPhMe$_2$)$_2$L]X (L = CNMe, C(NMeH)$_2$, C(NMeH)NMe$_2$, C(OMe)NMeH, C(OEt)NMeH, C(OMe)NMe$_2$, and C(OMe)$_2$; X = SO$_3$F, ClO$_4$, and PF$_6$) and *trans*-C$_6$Cl$_5$Ni(PPhMe$_2$)$_2${C(OMe)=NMe} have been prepared. The configuration of these complexes has been assigned on the basis of their ^{1}H NMR and IR spectra. Their electronic spectra showed a so-called d–d band, and the spectrochemical series of the carbene ligands was discussed with regard to the Ni–C π-bonding properties.

Introduction

There have been extensive studies of the syntheses, spectroscopic properties, and reactivities of transition metal carbene complexes, but reports of nickel carbene complexes are still uncommon compared with reports of palladium and platinum complexes.[1,2] As we previously reported,[3-6] a (pentachlorophenyl)nickel(II) moiety forms a variety of stable cationic complexes of type *trans*-[C$_6$Cl$_5$Ni(PPhMe$_2$)$_2$L]$^+$ (L = neutral ligand), as well as neutral complexes of types *trans*-C$_6$Cl$_5$Ni(PPhMe$_2$)$_2$X (X = anionic group) and *trans*-C$_6$Cl$_5$Ni(PPhMe$_2$)$_2$R (R = organic group), and we have recently reported[7,8] the syntheses of a series of stable cationic carbene complexes of types *trans*-[C$_6$Cl$_5$Ni(PPhMe$_2$)$_2${C(OR′)Me}]$^+$ and *trans*-[C$_6$Cl$_5$Ni(PPhMe$_2$)$_2${C(OMe)C$_6$H$_4$Y-*p*}]$^+$. Characteristic for these nickel complexes is the observation in the electronic spectrum of a band attributable to the so-called d–d transition.[5,6,8] We present here additional examples of stable cationic carbene complexes of the same nickel moiety and investigate the spectrochemical series of carbene ligands with a hope to elucidate their bonding properties.

Experimental Section

Since methyl fluorosulfonate has been cited[9] to be extremely toxic, experimental work using this reagent was performed in a hood. The commercial grade reagent was used after distillation under a nitrogen atmosphere. IR spectra were recorded on a Hitachi 225 spectrophotometer or on a Hitachi 215 spectrophotometer over the range 4000–650 cm^{-1} and on a Hitachi EPI-L spectrophotometer over the