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^{1}H AND ^{199}Hg NMR SPECTRA OF METHYLMERCURY(II) COMPLEXES. EFFECTS OF BASICITY AND ORTHO SUBSTITUTION IN PYRIDINES(L) IN COMPLEXES [MeHgL]NO_3

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Summary

Linear complexes [MeHgL]NO_3 (L = substituted pyridine) have been prepared and their ^{1}H and ^{199}Hg NMR spectra measured and compared with other complexes of this series reported previously. The coupling constant $J(^1H-^{199}Hg)$ correlates directly with pKa and with the gas phase enthalpy of ionization [$\Delta G_i(g)$] of LH^+; with $J(^1H-^{199}Hg)$ decreasing with increasing pKa or $\Delta G_i(g)$. The chemical shift, δ, for ^{199}Hg does not correlate with either pKa or $\Delta G_i(g)$. Complexes without substituents in the 2 position of pyridine have δ^{199}Hg ca. 80-100 ppm downfield from $MeHgNO_3$, those with one methyl group in the 2 position ca. 125-150 ppm, and those with methyl groups in the 2 and 6 position (or benzyl or 3'-methylpyridyl groups in the 2 position) ca. 160-200 ppm downfield from $MeHgNO_3$. The coupling constant $J(^1H-^{199}Hg)$ is found to be more useful than δ^{199}Hg in determination of solution structures of MeHg(II) complexes of this type of ligand.

Introduction

^1H nuclear magnetic resonance spectroscopy may be used to determine the coordination number of methylmercury(II) in closely related complexes $[MeHgL]NO_3$ (L = pyridines, 2,2'-bipyridyls) from an analysis of chemical shifts of the $H_{3,3'}$ and $H_{5,5'}$ protons of 2,2'-bipyridyls and from correlations between $J(^1H-^{199}Hg)$ and pKa of LH^+ [1]. For example, 3,3'-dimethyl-2,2'-bipyridyl (3,3'-dmbpy) forms a complex with one uncoordinated ring in the solid state [2] and in methanol the complex has a coupling constant consistent with presence of 3,3'-dmbpy as a unidentate ligand** [Fig. 1(a)]. Other 2,2'-bipyridyls form complexes with coupling constants 4-15 Hz higher indicating chelation [1], as found in the solid state for $[MeHg(2,2'\text{-bipyridyl})]NO_3$ [3]. In exploring the possible use of ^{199}Hg NMR spectroscopy for this purpose [6] we noticed that the ^{199}Hg resonance is not only sensitive to coordination number of mercury, but also to substitution in the 2 position of pyridines.

We have extended the series of linear complexes to study these effects further, and to estimate the relative merits of ^1H and ^{199}Hg NMR spectroscopy for determination of the coordination environment in MeHg(II) complexes of this type.

Experimental

The ligands 2,3-dimethylpyridine, 2,3,6-trimethylpyridine, and 5-ethyl,2-methylpyridine (Aldrich), 3,4-dimethylpyridine and 3,5-dimethylpyridine (Halewood), 2,4,6-trimethylpyridine (Ega-Chemie), and 3-ethyl, 4-methylpyridine (Fluka) were refluxed and distilled from KOH before use. The preparation of methylmercuric nitrate has been described previously [1]. Infrared spectra of complexes in Nujol mulls

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** Ionic structures $[MeHgL]NO_3$ in the solid state [1-4] are retained in methanol, e.g. $[MeHg(3\text{-Et},4\text{-mpy})]NO_3$ has molar conductance 85.5 ohm^{-1} mol^{-1} cm^2, within the range 80-115 ohm^{-1} mol^{-1} cm^2 expected [5] for 1:1 electrolytes in methanol.

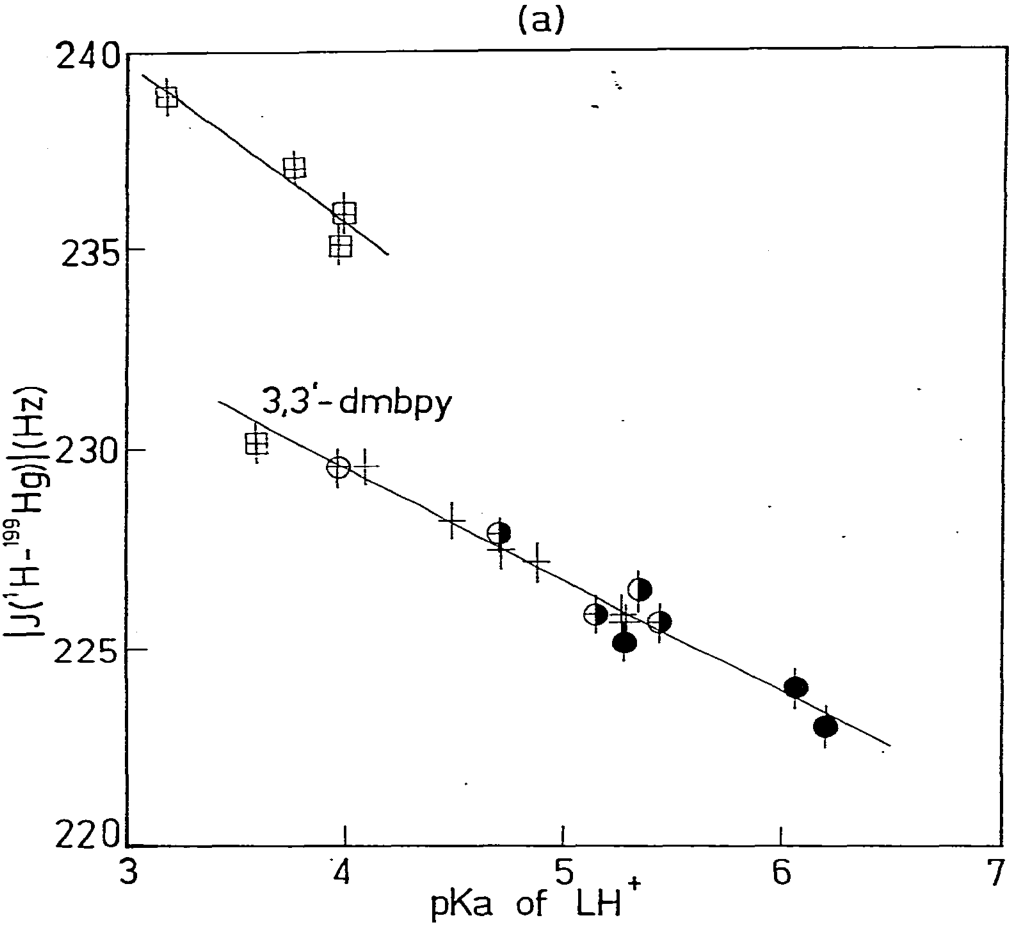

Fig. 1. Full legend see p. 451.

were recorded with a Perkin-Elmer 577 spectrophotometer. Apparent protonation constants of the above ligands were measured as described previously [1]. Complexes were precipitated from acetone solutions of methylmercuric nitrate and ligand in equimolar ratio at ambient temperature. For the 3,5-dimethylpyridine, 5-ethyl, 2-methylpyridine, and 2,4,6-trimethylpyridine complexes evaporation to low volume was required before crystallization occurred. Moderate yields (24-92%) were obtained. Characterization data for the new complexes are given in Table 1. ^{1}H and ^{199}Hg NMR spectra were recorded as described previously [1,6], and are given in Tables 2 and 3.

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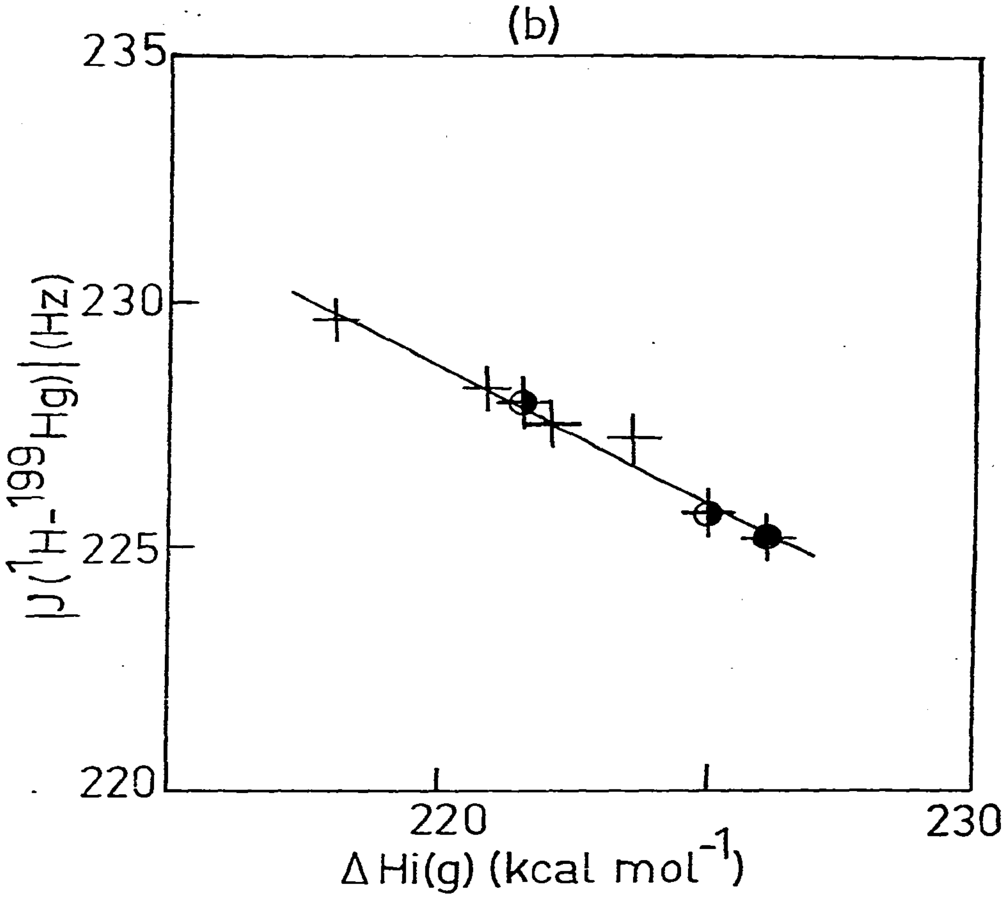

TABLE 1

ANALYTICAL DATA FOR THE NEW COMPLEXES

Complex	% calcd.			% found		
	C	H	Hg	C	H	Hg
[MeHg(2,3-dmpy)]NO_3[a]	25.0	3.1	52.1	24.8	3.2	51.7
[MeHg(3,4-dmpy)]NO_3[a]	25.0	3.1	52.1	25.1	3.3	51.2
[MeHg(3,5-dmpy)]NO_3.½H_2O[b]	24.4	3.3	50.9	24.5	3.3	51.0
[MeHg(2,4,6-tmpy)]NO_3[c]	27.1	3.5	50.3	26.9	3.7	50.0
[MeHg(2,3,6-tmpy)]NO_3	27.1	3.5	50.3	27.6	3.6	50.0
[MeHg(5-Et,2-mpy)]NO_3	27.1	3.5	50.3	27.5	3.6	49.9
[MeHg(3-Et,4-mpy)]NO_3	27.1	3.5	50.3	27.3	3.5	49.9

[a] ν(Hg-C) 559 cm^{-1}. [b] Calc. N, 7.1. Found 7.1%. Water absorption at 3420m(vbr). ν(Hg-C) 563 cm^{-1}. [c] Recryst. from ethanol.

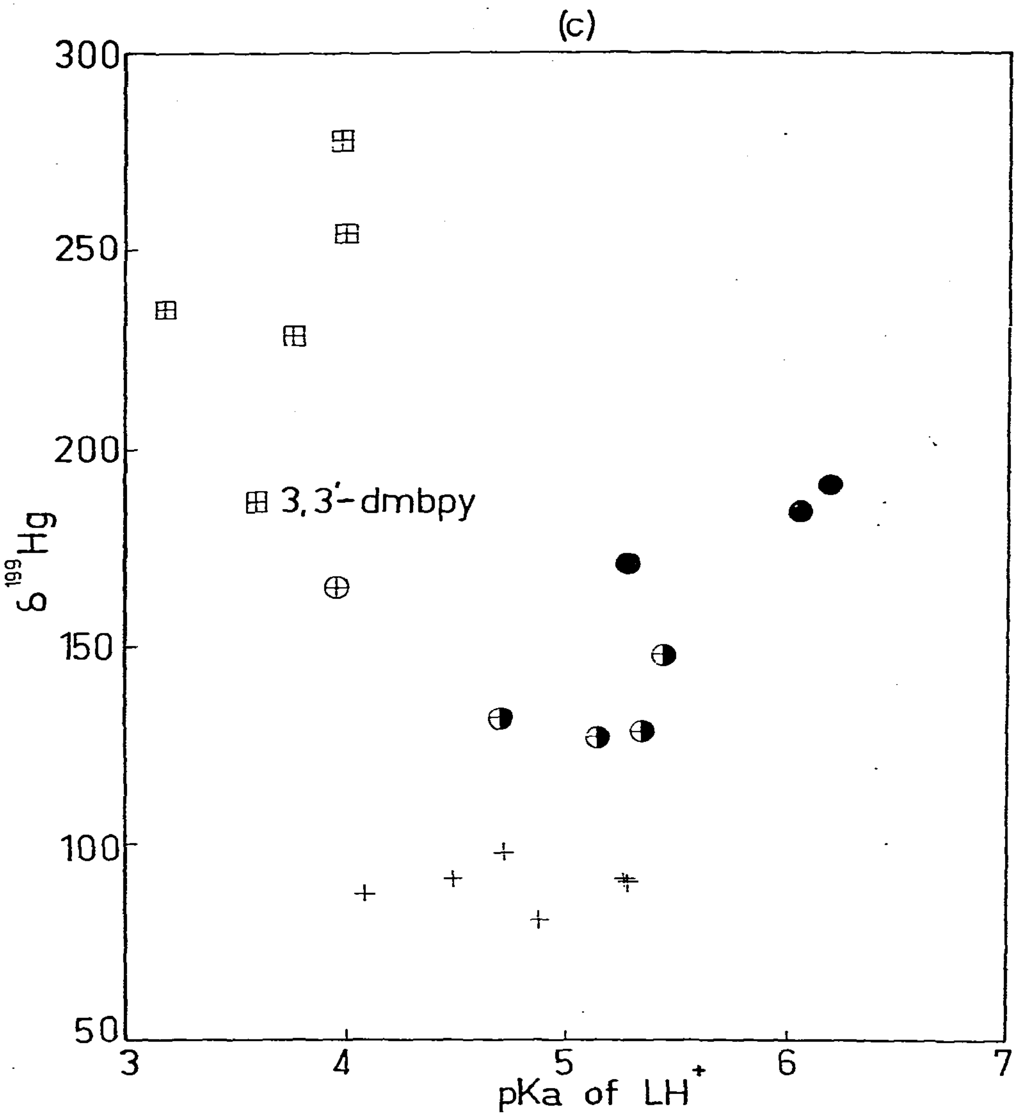

Fig. 1. Relationship between (a) $|J(^1H-^{199}Hg)|$ and pKa of LH^+; (b) $|J(^1H-^{199}Hg)|$ and gas phase enthalpy of ionization of LH^+, $\Delta H_i(g)$, $|J(^1H-^{199}Hg)| = -0.55\Delta H_i(g) + 229.7$ Hz, correl. coefft. -0.99; (c) $|J(^1H-^{199}Hg)|$ and δ^{199}Hg in the complexes $[MeHgL]NO_3$, where L = pyridines without substituents in the 2 position (+), 2-benzylpyridine (ɸ), pyridines with a methyl group in the 2 position (◑), pyridines with methyl groups in the 2 and 6 positions (●), and 2,2'-bipyridyls (⊞).

TABLE 2

^{1}H NMR DATA FOR THE NEW COMPLEXES[a]

Complex	Me_{Hg}	Ligand protons						Coupl const within ligand
		H_2	H_3	H_4	H_5	H_6	R	
[MeHg(2,3-dmpy)]NO_3	-2.52			4.37dd	ca.3.99m	4.84dd	-0.84(2) -1.21(3)	$J_{4,5}$ = 7.8; $J_{5,6}$ = 4.9; $J_{4,6}$ = 1.6
[MeHg(3,4-dmpy)]NO_3	-2.59	ca.4.80m			4.00d	ca.4.77m	-1.20, -1.27	$J_{5,6}$ = 5.6
[MeHg(3,5-dmpy)]NO_3.½H_2O	-2.58	4.68		4.26		4.68	-1.22	
[MeHg(2,4,6-tmpy)]NO_3	-2.48		3.78		3.78		-0.52(2,6), -1.21(4)	
[MeHg(2,3,6-tmpy)]NO_3	-2.47			4.25d	3.80d		-0.83, -0.85	$J_{4,5}$ = 7.6
[MeHg(5-Et,2-mpy)]NO_3	-2.53		4.01d	4.36dd		4.86d	-0.83(2), -0.88q(CH_2) -1.36t(Me)	$J_{3,4}$ = 8.2; $J_{4,6}$ = 2.1; J(Et) = 7.6
[MeHg(3-Et,4-mpy)]NO_3	-2.58	4.83			4.02d	4.75d	-1.15(4), -0.84q(CH_2), -2.36t(Me)	$J_{5,6}$ = 5.8; J(Et) = 7.5

[a] Solutions 0.1M in CD_3OD. Chemical shift from internal 1,4-dioxane, shifts upfield of 1,4-dioxane are taken as negative.

TABLE 3

NMR PARAMETERS FOR THE METHYLMERCURY GROUP IN COMPLEXES [MeHgL]NO_3, TOGETHER WITH pKa of LH^+ AND THE GAS PHASE ENTHALPY OF IONIZATION OF LH^+ [$\Delta H_i(g)$]

Complex	$\lvert J(^1H-^{199}Hg)\rvert$[a]	$\delta^{199}Hg$[b]	pKa of LH^+[c]	$\Delta H_i(g)$[d]
$MeHgNO_3$	251.8[e]			
[MeHg(py)]NO_3	229.6[e]	87.0[f]	4.09[e]	218.1
[MeHg(2-mpy)]NO_3	227.9[e]	132.0[f]	4.71[e]	221.6
[MeHg(3-mpy)]NO_3	228.2[e]	91.0[f]	4.49[e]	220.8
[MeHg(4-mpy)]NO_3	227.5[e]	98.0[f]	4.72[e]	222.1
[MeHg(2,3-dmpy)]NO_3[g]	226.5	128.5	5.35	
[MeHg(2,4-dmpy)]NO_3	225.7[e]	148.0[f]	5.44[e]	225.0
[MeHg(2,6-dmpy)]NO_3	225.2[e]	171.0[f]	5.28[e]	226.1
[MeHg(3,4-dmpy)]NO_3	225.9	90.8	5.27	
[MeHg(3,5-dmpy)]$NO_3.\frac{1}{2}H_2O$	227.2	80.6	4.88	223.6
[MeHg(2,4,6-tmpy)]NO_3[g]	223.0	191.0	6.20	
[MeHg(2,3,6-tmpy)]NO_3	224.0	184.3	6.06	
[MeHg(5-Et,2-mpy)]NO_3	225.9	127.0	5.15	
[MeHg(3-Et,4-mpy)]NO_3	225.7	90.4	5.28	
[MeHg(2-Bzlpy)]NO_3[g]	229.6[e]	165.0[f]	3.97[e]	
[MeHg(bpy)]NO_3	238.8[e]	236[f]	3.18[e]	
[MeHg(6,6'-dmbpy)]$NO_3.H_2O$	235.9[e]	255[f]	3.99[e]	
[MeHg(5,5'-dmbpy)]NO_3	237.0[e]	229[f]	3.76[e]	
[MeHg(4,4'-dmbpy)]NO_3	235.1[e]	278[f]	3.97[e]	
[MeHg(3,3'-dmbpy)]NO_3[g]	230.4[e]	187[f]	3.59[e]	

[a] 0.1M solutions in CD_3OD at 100 MHz. Accuracy to ca. ± 0.5 Hz. The sign of the coupling constant is assumed to be negative [7]. [b] ca. 0.1M solutions in CH_3OH. Shifts are downfield from $MeHgNO_3$, accuracy to ± 2 ppm. ^{199}Hg resonance frequencies of individual samples were measured at constant field strength and shifts were calculated from the formula $\sigma = [\nu(sample) - \nu(MeHgNO_3)]/\nu(MeHgNO_3)$. The ^{199}Hg resonance frequency of $MeHgNO_3$ under the conditions of the experiment was 16.099556 MHz. All samples resonated at higher frequencies than $MeHgNO_3$; corresponding to a 'downfield shift' observed by standard constant frequency/variable field NMR experiments. [c] Accuracy to ca. ± 0.05. [d] In kcal mol^{-1}, from ref. 8,9. Values of $\delta\Delta H_i(g)$, the gas phase enthalpy change for the isodesmic proton transfer from the substituted pyridinium ion ($XpyH^+$) to pyridine.

$$XpyH^+ + py \rightarrow Xpy + pyH^+ \text{ (gas)}$$

have been placed on the scale of absolute proton affinities by taking pyridine as 218.1 kcal mol^{-1} [9]. Accuracy of $\delta\Delta H_i(g)$ estimated to be ± 0.2 kcal mol^{-1} [8,9]. [e] From ref. 1. [f] From ref. 6 where these values were incorrectly reported as upfield from $MeHgNO_3$. [g] 2,3-dmpy = 2,3-dimethylpyridine, 2,4,6-tmpy = 2,4,6-trimethylpyridine, 2-Bzlpy = 2-benzylpyridine, 3,3'-dmbpy = 3,3'-dimethyl-2,2'-bipyridyl, other ligands similarly abbreviated.

Results and Discussion

1. ^{1}H NMR spectra

The additional ^{1}H NMR data from the new complexes, and pKa determinations for the ligands used in their synthesis, confirm the linear relationship between $J(^1H-^{199}Hg)$ and basicity of the pyridine donor, represented by apparent pKa of LH^+ measured in 50% dioxane-water: $J(^1H-^{199}Hg) = -2.83pKa + 240.9$ Hz with correl. coefft. -0.98 [Fig. 1(a)]. This solvent mixture was chosen for pKa determinations in initial studies [1] to allow comparison of results for water insoluble ligands, but similar linear relationships occur for pKa's measured in water***, and other measures of relative basicity such as gas phase enthalpies of ionization of LH^+, $\Delta H_i(g)$, which are available for seven of the pyridines studied here [8,9] (Table 3, Fig. 1(b)). The cause of the increase in coupling constants with decreasing basicity of the pyridine donor has been discussed earlier on the basis that the relative magnitude of $J(^1H-^{199}Hg)$ is due mainly to the Fermi contact mechanism [1].

The $J(^1H-^{199}Hg)$ vs pKa trend has assisted with assignment of binding sites of MeHg(II) to the nucleoside guanosine [13] and, for the pyridine and 2,2'-bipyridyl complexes, confirmation of structural assignment using $J(^1H-^{199}Hg)$ sometimes comes from the chemical shift of the MeHg(II) proton when the ligand has an aromatic ring that can shield the MeHg(II) proton. Thus, the ^{1}H resonance for the MeHg(II) group in [MeHg(3,3'-dmbpy)]NO_3 and [MeHg(2-benzylpyridine)]NO_3 are shifted 0.2-0.4 ppm upfield from other pyridine and 2,2'-bipyridyl complexes [1], consistent with the presence of an aromatic ring in an orientation such that the methyl group

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*** Plots of coupling constants vs pKa values are sensitive to the conditions under which pKa values are measured because of the small change in $J(^1H-^{199}Hg)$ with pKa and variation in reported pKa values, e.g. values for pyridine in water range from 5.15-5.52 [10]. However, values for the first 10 pyridines in Table 3 in water have been reported by the same workers under identical conditions [11] and these values give a line $J(^1H-^{199}Hg) = -2.80pKa + 244.3$ Hz with correl. coefft. -0.99, and values of Andon et al. [12] for the first 9 pyridines in water give $J(^1H-^{199}Hg) = -2.71pKa + 243.7$ Hz with correl. coefft. -0.98.

is shielded by the ring current anisotropy [1]. Similar effects occur in other MeHg(II) complexes [14-17] and have been confirmed by crystal structures for $MeHg\overset{+}{N}H_2CH(CO_2^-)CH_2$(p-OHPh) [18] and [MeHgL]NO_3 (L = 3,3'-dmbpy [2] and 2-benzylpyridine [19]). Orientation of the rings in this manner apparently results from weak π-interaction between mercury and the rings [2,16,19].

2. ^{199}Hg NMR spectra

The additional ^{199}Hg NMR data indicate that, contrary to earlier results obtained from a smaller number of complexes [6], there is not a direct correlation between δ^{199}Hg and pKa of pyridines [Fig. 1(c)]. For example, complexes of py and 3-Et,4-mpy have δ^{199}Hg within experimental error (±2 ppm), 87.0 and 90.4 ppm <u>downfield</u> from $MeHgNO_3^{\dagger}$ for pKa values 4.09 and 5.28, respectively, while 2-mpy has δ^{199}Hg 132.0 ppm for an intermediate pKa value of 4.71. Instead, in the plot of δ^{199}Hg vs pKa, the complexes of pyridines fall into three groups - those without substituents in the 2 position (+, ca. 80-100 ppm downfield from $MeHgNO_3$), those with one Me group in the 2 position (⊕, ca. 125-150 ppm), and those with Me groups in the 2 and 6 positions (●) or benzyl or 3'-methylpyridyl groups in the 2 position (ca. 160-200 ppm).

The additional downfield shift resulting from substitution in the 2 and 6 positions could conceivably arise from either an alteration in C-Hg-N bonding at mercury, or from a 'solvent effect' as addition of organic groups at the 2 and 6 positions effectively alters the solvent environment around mercury. The 2-mpy complex has a stability constant log K 4.35 [20], lower than that of py (4.72 [21], 4.8 [22]), 3-mpy (4.69 [20], and 4-mpy (5.03 [20]), but crystal structures of two complexes having bulky substituents in the 2 position, [MeHg(3,3'-dmbpy)]NO_3 [2] and [MeHg(2-Bzlpy)]NO_3 [19] (2-Bzlpy = 2-benzylpyridine), suggest that steric interaction between mercury and substituents in the 2 position

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[†] Chemical shifts were incorrectly reported as upfield from $MeHgNO_3$ in ref. 6.

does not alter the coordination geometry at mercury from that in [MeHg(py)]NO_3. These complexes have Hg-N(1) 2.11(1) and 2.10(2) Å, respectively; values identical with that in [MeHg(py)]NO_3, 2.12(2) Å [4]. As well, the substituted coordinated pyridine rings are not bent away from the Hg-N(1) direction, whereas some form of distortion might be expected if significant steric interaction existed[††]. The mercury atom is coplanar with the coordinated ring in the pyridine complex, but 0.006(1) and 0.060(1) Å out of the plane in the 3,3'-dmbpy and 2-Bzlpy complexes, respectively. Both the py and 2-Bzlpy complexes have linear C-Hg-N(1), 179.7(6) and 180(1)° respectively, and the angle of 172.7(5)° for the 3,3'-dmbpy complex results from weak Hg...O interactions with the methyl group bent away from the nitrate ion towards the pyridyl ring in the 2 position. Although changes in $J(^1H-^{199}Hg)$ with a small alteration from linearity are expected to be less than that observed on increase of coordination number with bidentate 2,2'-bipyridyls, any alteration of coordination geometry from linearity in [MeHg(py)]NO_3 would be expected to shift values of $J(^1H-^{199}Hg)$ for 2 and 6 substituted pyridines away from the linear $J(^1H-^{199}Hg)$ vs basicity relationships in Figures 1(a) and 1(b).

It is well known that the ^{199}Hg chemical shift in organomercury compounds is sensitive to solvent conditions [23-27], e.g. for Me_2Hg solvents such as pyridine and dimethylsulphoxide can affect shielding by up to 100 ppm [25]. The 'solvent environment' for mercury is expected to be altered by substitution at the 2 position of pyridine as it is constrained by the complex geometry to be close to the mercury atom. The mercury environment would be rendered less polar with the presence of a non-polar organic substituent within the first coordination sphere. As well, the possibility of acid-base interactions between the mercury atom and the solvent methanol molecules or the nitrate counterion weak Hg...NO_3 interaction is present in the crystal structure of [MeHg

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[††] Hg-N(1)-C(2,6) angles are within 2σ of 120° in the 3,3'-dmbpy and 2-Bzlpy complexes.

(3,3'-dmbpy)]NO_3 [2] - may be considerably reduced by the presence of the substituent. Such effects appear sufficient to mask any dependence of the ^{199}Hg chemical shift on ligand pKa.

3. Comparison of ^{1}H and ^{199}Hg NMR spectra

^{1}H NMR spectra of complexes of pyridines and 2,2'-bipyridyls are useful for assignment of coordination number of MeHg(II). Complexes of chelating 2,2'-bipyridyls have ^{199}Hg chemical shifts different from unidentate pyridines [Fig. 1(c)], but the extreme sensitivity of the ^{199}Hg chemical shift to essentially non-bonding effects suggests that for the determination of coordination number of MeHg(II) in complexes of related ambidentate or potentially multidentate nitrogen donor ligands the readily measured coupling constant may be more reliable. However, for these complexes, and other MeHg(II) compounds [27], ^{199}Hg NMR spectra provide useful information about the coordination number of mercury and interaction of mercury with the solvent.

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