that the exchange interaction is greatly affected by the perchlorate coordination. The observed effect could be produced in the following two ways. The additional coordination certainly acts as a perturbation on the electronic structure of the complex and could alter the electron density available to the hydroxo oxygen atoms and hence affect this superexchange mechanism. Alternatively, the perchlorate bridges could be integrally involved in the exchange interaction and provide an additional superexchange pathway. Although the former possibility could produce the observed effect, the analysis of the zero-field interaction lends some credence to the latter. Since the observed zero-field parameter has an unusually large contribution from the anisotropic exchange interaction, the possibility of a significant involvement of the perchlorate bridges in a superexchange mechanism cannot be excluded.

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Registry No. α-$[\mathrm{Cu(DMAEP)OH}]_2(\mathrm{ClO_4})_2$, 42476-26-6.

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Organomercury Compounds Containing Three-Coordinate Mercury. Synthesis and Spectroscopic Studies of Cationic Complexes of Methylmercury(II) with Neutral Donor Ligands

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Synthetic and spectroscopic studies of cationic complexes of methylmercury(II), $[\mathrm{MeHgL}][\mathrm{NO_3}]$, are reported. The complexes $[\mathrm{MeHgL}][\mathrm{NO_3}]$ (L = pyridine; 2-methyl-, 3-methyl-, 4-methyl-, 2-benzyl-, 2,4-dimethyl-, and 2,6-dimethylpyridine; 2,2'-bipyridyl; 3,3'-dimethyl-, 4,4'-dimethyl-, 5,5'-dimethyl-, and 6,6'-dimethyl-2,2'-bipyridyl; 1,10-phenanthroline; 2,9-dimethyl-, 4,7-dimethyl-, and 5,6-dimethyl-1,10-phenanthroline) are obtained from addition reactions in acetone. A complex of composition $\mathrm{MeHgNO_3}\cdot{}^1/_2\mathrm{L}$ is also formed by 3,3'-dimethyl-2,2'-bipyridyl. Infrared evidence for coordination of ligands in the solid complexes is presented. Proton magnetic resonance spectra indicate that the complexes of 2,2'-bipyridyls (except for those of 3,3'-dimethyl-2,2'-bipyridyl) and 1,10-phenanthrolines have three-coordinate mercury in solution. A linear correlation is observed between $J(^1\mathrm{H}-^{199}\mathrm{Hg})$ and protonation constants of the ligands, with separate relationships for complexes of unidentate ligands, bidentate 2,2'-bipyridyls, and 1,10-phenanthrolines. Aspects of bonding in three-coordinate complexes are deduced from ^{1}H and ^{13}C NMR of the complexes and an x-ray structural determination of $[\mathrm{MeHg(2,2'\text{-}bpy)}][\mathrm{NO_3}]$. Bonding between mercury and carbon in the three-coordinate complexes is considered to be similar to that in the linear sp-hybridized complexes of pyridine ligands. Comparison of structural data for the 2,2'-bipyridyl and some amino acid complexes of methylmercury suggests that a similar sp hybridization bonding model is applicable for the latter complexes.

A major feature of bonding in organomercury chemistry is the strong tendency for linear two-coordination for mercury.[1,2] Consequently, spectroscopic studies of bonding in organomercury chemistry have been restricted almost entirely to linear two-coordinate geometry in $\mathrm{R_2Hg}$, RHgX, and $[\mathrm{RHgL}][\mathrm{X}]$ (L = unidentate ligand). However, recent structural studies indicate that even the simplest organomercury cation, $\mathrm{MeHg^+}$, may achieve effective coordination numbers of 3 and 4 for mercury in the amino acid complexes $\mathrm{MeHg^+{-}NH_2CH(CO_2^-)CMe_2SHgMe}$[3] and $\mathrm{MeHg^+{-}NH_2CH(CO_2^-)CH_2CH_2SMe}$,[4] respectively. For the amine-bonded methylmercury groups the mercury–carboxylate oxygen contacts are only ca. 0.2 Å less than the sum of van der Waals radii and thus may be ionic interactions resulting from the zwitterionic nature of the complexes.[4] In view of the importance of these complexes in the biological chemistry of methylmercury pollutants an understanding of the bonding of mercury in methylmercury compounds with coordination number greater than 2 is desirable. NMR spectroscopy is particularly useful for bonding studies of methylmercury compounds[5,6] but may not be applicable for a study of methylmercury with coordination number of mercury greater than 2 in the above amino acid complexes because Rabenstein et al. have concluded from ^{1}H NMR studies that similar amino

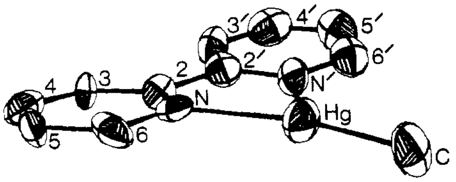


Figure 1. Structure of the planar cation $[\mathrm{MeHg(2,2'\text{-}bpy)}]^+$ in $[\mathrm{MeHg(2,2'\text{-}bpy)}][\mathrm{NO_3}]$.

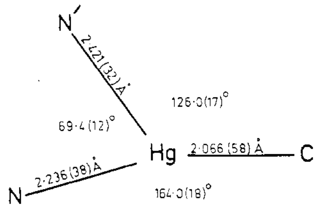


Figure 2. Stereochemistry of mercury in $[\mathrm{MeHg(2,2'\text{-}bpy)}][\mathrm{NO_3}]$.

acids act as unidentates toward $\mathrm{MeHg^+}$ in aqueous solution.[7]

We have reported the isolation (eq 1) and preliminary study

$$\mathrm{MeHgNO_3} + \mathrm{L} \rightarrow [\mathrm{MeHgL}][\mathrm{NO_3}] \qquad (1)$$

of a series of complexes $[\mathrm{MeHgL}][\mathrm{NO_3}]$ (L = 2,2'-bipyridyl, 1,10-phenanthroline, and related ligands) having three-coordinate mercury.[8] A crystal structure analysis shows that the 2,2'-bipyridyl complex has a planar $\mathrm{CHgN_2}$ group with unsymmetrically chelated 2,2'-bipyridyl (Figures 1 and 2).[8] Both mercury–nitrogen distances are significantly less than the sum of van der Waals radii (3.0 Å) and are similar to Hg–N distances in other 2,2'-bipyridyl complexes of mercury(II), e.g., 2.373 (9) and 2.399 (8) Å in $[\mathrm{HgBr_2(2,2'\text{-}bpy)}]_2$.[9] The complex $[\mathrm{MeHg(2,2'\text{-}bpy)}][\mathrm{NO_3}]$ was initially prepared by Coates and Lauder,[10] and stability constant studies suggest that 2,2'-bipyridyl and 1,10-phenanthroline are chelated to $\mathrm{MeHg^+}$ in aqueous solution.[11] Since many detailed ^{1}H NMR spectroscopic studies of 2,2'-bipyridyls, 1,10-phenanthrolines, and linear methylmercury compounds[5,6] have been reported, a similar study of this series of complexes together with related complexes having two-coordinate mercury, $[\mathrm{MeHgL}][\mathrm{NO_3}]$ (L = pyridine and related ligands), may give an indication of the nature of bonding in three-coordinate organomercury compounds.

Experimental Section

Preparation of Compounds. The ligands 6,6'-dimethyl-, 5,5'-dimethyl-, and 3,3'-dimethyl-2,2'-bipyridyl were prepared by published methods.[12] All other ligands are commercially available and were used as received. Methylmercuric nitrate was prepared from methylmercuric chloride and silver nitrate[13] and was recrystallized from water.

Complexes were obtained in moderate yield (33–84%) following the general procedure used by Coates and Lauder[10] and Goggin et al.[14] in preparation of $[\mathrm{MeHg(2,2'\text{-}bpy)}][\mathrm{NO_3}]$ and $[\mathrm{MeHg(py)}][\mathrm{NO_3}]$, respectively (eq 1). All of the complexes precipitated from acetone solutions of methylmercuric nitrate and ligand in appropriate stoichiometric ratios and, except for complexes of dimethylpyridines and 3,3'-dimethyl-2,2'-bipyridyl (highly crystalline from acetone) and those of 1,10-phenanthrolines (low solubility), were recrystallized from 95% ethanol. Complexes were prepared at ambient temperature and their solutions were not heated during recrystallization. Complexes of 6,6'-dimethyl-2,2'-bipyridyl and 2,9-dimethyl-1,10-phenanthroline crystallized as monohydrates, and water could not be removed from them with phosphorus pentoxide as desiccant. Microanalyses were by the Australian Microanalytical Service, Melbourne. The complexes isolated and their characterization data are summarized in Table I.

Physical Measurements. Infrared spectra (4000–400 cm^{-1}) of complexes in Nujol and hexachlorobutadiene mulls and far-infrared spectra (400–200 cm^{-1}) of complexes in Nujol mulls between polyethylene plates were recorded with a Perkin-Elmer 577 spectrophotometer.

^{1}H NMR spectra at 100 MHz were measured on a JEOL JNM-4H-100 spectrometer. Chemical shifts of 0.1 *M* solutions in $\mathrm{CD_3OD}$ were measured relative to 1,4-dioxane internal standard; shifts upfield of 1,4-dioxane are taken as negative. ^{1}H NMR spectra of the 4,7-dimethyl- and 5,6-dimethyl-1,10-phenanthroline complexes, which are insufficiently soluble for CW ^{1}H NMR spectroscopy, were obtained by the pulsed Fourier transform (PFT) technique with a Bruker WH-90 spectrometer. ^{13}C NMR spectra were obtained with JEOL PS-100 PFT and Bruker HX-90 instruments with noise-modulated proton decoupling. ^{1}H NMR data are summarized in Table II.

Apparent protonation constants K_{H} of all ligands were measured by the method of Albert and Serjeant[15] and are given with Figure 3. Since some of the ligands have low solubility in water and literature values are available for several in 50% 1,4-dioxane–water, protonation constants were measured in this solvent mixture. Dioxane was purified[16] in the following ways: (i) refluxing for 4 hr with concentrated HCl (dioxane:HCl = 5:2), neutralizing the solution with $\mathrm{Na_2CO_3}$, and adding KOH until no more dissolved; (ii) decanting off the dioxane, refluxing over KOH for 2 hr, and then distilling from freshly added KOH. The pyridines were distilled from KOH. Titration of 0.01 *M* solutions of ligand with aqueous 0.1 *M* HCl at 20 ± 1°C were monitored with a Pye Unicam Model 290 Mk2 pH meter. Precautions were taken to prevent evaporation during titrations, and the dioxane:water ratio at the midpoint of the buffer region was arranged to be 1:1 by volume. Corrections for activity were not made and the accuracy of the apparent protonation constants is considered to be ca. ±0.05 log K_{H} unit. Values for ligands whose protonation constants have been previously reported were consistently low by 0.2–0.5 unit from literature values (see Figure 3).

Results

Solid-State Structures. Coordination of ligands in the solid state can be ascertained from ir spectral data. Ir spectra indicate the presence of methylmercury, nitrate, and ligand moieties with ir absorptions altered from those of the free ligand and methylmercuric nitrate.

Very strong broad absorptions in the region 1392–1300 cm^{-1} are characteristic of uncoordinated nitrate ions,[21] as found in the crystal structure analysis of the 2,2'-bipyridyl complex.[8] A weak nitrate absorption near 1750 cm^{-1} indicates that some $\mathrm{KNO_3}$ from ion exchange with the KBr plates is also present in Nujol mulls of the 2,4-dimethyl- and 2,6-dimethylpyridine complexes.[22]

For most of the complexes ν(Hg–C) can be readily assigned (Table I) and, if the uncertain assignments are excluded, ν(Hg–C) for complexes of the 2,2'-bipyridyls (537–549 cm^{-1}) and 1,10-phenanthrolines (534–554 cm^{-1}) fall in a similar range (546 ± 9 cm^{-1}) slightly lower than but overlapping that of the pyridine complexes (560 ± 12 cm^{-1}).

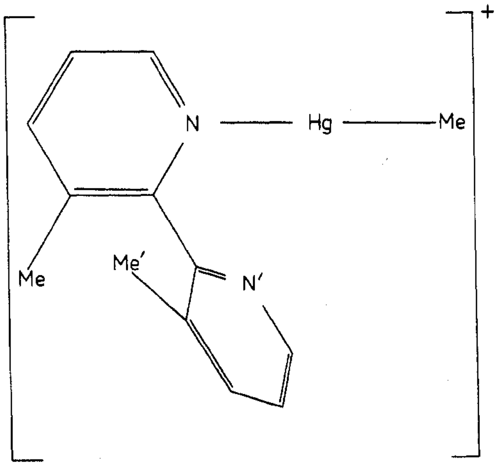
Characteristic shifts to higher energy observed on coordination of pyridine,[23] 2,2'-bipyidyl,[24,25] and 1,10-phenanthroline[25] occur in complexes of these ligands; e.g., free ligand bands near 400 and 600 cm^{-1} are raised 18–19 and 9–51 cm^{-1}, respectively, in the complexes. Similar shifts of 2–28 and 7–34 cm^{-1}, respectively, occur for absorptions in these regions in complexes of the other pyridines, 2,2'-bipyridyls and 1,10-phenanthrolines.[26]

However, although these shifts in ligand absorption indicate *coordination*, they do not necessarily indicate *chelation* to give three-coordinate mercury for the 2,2'-bipyridyl complexes where unidentate coordination is possible; e.g., ir spectra indicate that 3,3'-dimethyl-2,2'-bipyridyl (3,3'-dmbpy) is coordinated in $[\mathrm{MeHg(3,3'\text{-}dmbpy)}][\mathrm{NO_3}]$ although excessive steric interaction between the 3- and 3'-methyl groups cannot allow a cis conformation of the ligand required for chelation. Thus, ^{1}H NMR spectra (see below) indicate unidentate coordination in solution (I) but in the solid state other structures, e.g., bridging bidentate, $[-(\mathrm{MeHg^+})\text{–}\mathrm{N}\sim\mathrm{N}\text{–}]_n[\mathrm{NO_3}]_n$, cannot be excluded. The compound of composition $\mathrm{MeHgNO_3}\cdot{}^1/_2(3,3'\text{-dmbpy})$ has a different ir spectrum from that of $[\mathrm{MeHg(3,3'\text{-}dmbpy)}][\mathrm{NO_3}]$ and may well have a bridging

Table I. Characterization Data for $[MeHgL][NO_3]$

Complex	% calcd				% found				ν(Hg–C), cm^{-1}
	C	H	Hg	N	C	H	Hg	N	
$[MeHg(py)][NO_3]$[a]	20.20	2.26	56.23	7.85	20.61	2.27	55.60	7.43	563[e]
$[MeHg(2\text{-mpy})][NO_3]$	22.68	2.72	54.10	7.56	22.91	2.73	53.60	7.37	559
$[MeHg(3\text{-mpy})][NO_3]$	22.68	2.72	54.10	7.56	22.60	2.90	54.10	7.29	566
$[MeHg(4\text{-mpy})][NO_3]$	22.68	2.72	54.10	7.56	22.97	2.50	54.30	7.45	564
$[MeHg(2,4\text{-dmpy})][NO_3]$	24.97	3.14	52.13	7.28	24.72	3.25	51.70	7.59	564
$[MeHg(2,6\text{-dmpy})][NO_3]$	24.97	3.14	52.13	7.28	24.96	3.16	51.80	7.23	f
$[MeHg(2\text{-Bzlpy})][NO_3]$	34.94	3.16	44.89	6.27	34.87	3.14	44.60	6.40	548
$[MeHg(bpy)][NO_3]$[b]	30.46	2.56	46.24	9.69	30.35	2.49	45.50	10.19	547[g]
$[MeHg(6,6'\text{-dmbpy})][NO_3]\cdot H_2O$[c]	32.54	3.57	41.80	8.76	32.57	3.36	41.60	8.94	537
$[MeHg(5,5'\text{-dmbpy})][NO_3]$	33.81	3.27	43.43	9.10	33.58	3.20	43.20	8.90	549
$[MeHg(4,4'\text{-dmbpy})][NO_3]$	33.81	3.27	43.43	9.10	33.49	3.36	43.30	9.10	540, 562[h]
$[MeHg(3,3'\text{-dmbpy})][NO_3]$	33.81	3.27	43.43	9.10	33.86	3.17	43.10	8.93	550
$MeHgNO_3\cdot{}^1/_2(3,3'\text{-dmbpy})$	22.74	2.45	54.25	7.58	22.70	2.45	53.80	7.42	561, 549[i]
$[MeHg(phen)][NO_3]$	34.10	2.42	43.81	9.18	33.89	2.32	43.40	9.11	
$[MeHg(2,9\text{-dmphen})][NO_3]\cdot H_2O$[d]	35.75	3.40	39.81	8.34	36.26	3.27	39.80	8.06	554
$[MeHg(4,7\text{-dmphen})][NO_3]$	37.08	3.11	41.28	8.65	36.78	3.05	41.10	8.58	545
$[MeHg(5,6\text{-dmphen})][NO_3]$	37.08	3.11	41.28	8.65	36.86	3.05	40.90	8.65	543[j]

[a] py = pyridine. [b] bpy = 2,2'-bipyridyl. [c] 6,6'-dmbpy = 6,6'-dimethyl-2,2'-bipyridyl. [d] 2,9-dmphen = 2,9-dimethyl-1,10-phenanthroline. Other ligands are similarly abbreviated. [e] Literature[14] value 562 cm^{-1}. [f] There are several bands in the region 500–600 cm^{-1}, thus assignment is not possible. [g] Literature[10] value 545 cm^{-1}. [h] Assignment is uncertain; one of these may be a ligand absorption. [i] Since the structure of this compound is uncertain, there may be either two methylmercury environments or one environment with one of these absorptions as a ligand mode. [j] The ligand has a band in this region; thus this band may cover a coincident or nearby ν(Hg–C) absorption.



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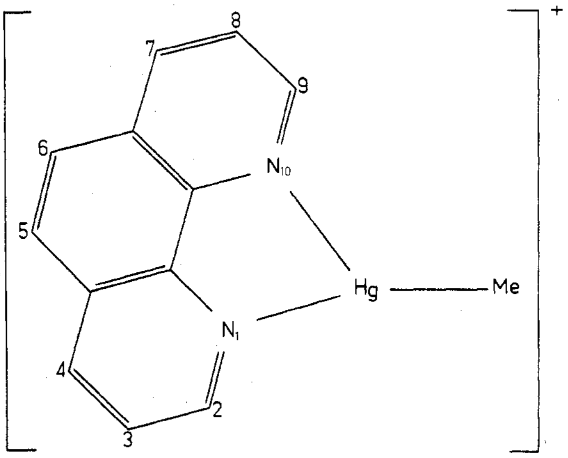

II

ligand, $[MeHg\text{–}N{\sim}N\text{–}HgMe]^{2+}$, although ^1H NMR spectra (see below) indicate that in solution it forms an equimolar mixture of $[MeHg(3,3'\text{-dmbpy})][NO_3]$ and $MeHgNO_3$. Complexes involving the other 2,2'-bipyridyls and 1,10-phenanthrolines are assumed to have structures similar to that of the 2,2'-bipyridyl complex (Figures 1 and 2).

Nuclear Magnetic Resonance Spectra. ^1H NMR spectra of the complexes are readily assigned, and values of chemical shifts and coupling constants obtained from first-order analysis[19] are given in Table II. Integrated intensities in ^1H NMR spectra are as required for formulas presented. The presence of the rapid equilibrium

$$MeHg^+ + L \rightleftharpoons [MeHgL]^+$$

with observed spectra resulting from coalescence of resonances of $MeHg^+$, L, and $[MeHgL]^+$ is not expected to alter the spectra from that of $[MeHgL]^+$ since stability constants for formation of the pyridine, 2,2'-bipyridyl, and 1,10-phenanthroline complexes in aqueous solution are appreciable ($\log K = 4.8$,[27] 5.86,[11] and 7.15,[11] respectively).[28] For 2,2'-bipyridyl and 1,10-phenanthroline ligands the presence of rapid equilibrium ensures averaging of resonances for n and n' protons (Figure 1), and related protons in 1,10-phenanthroline complexes (II), if structures similar to that of $[MeHg(2,2'\text{-bpy})][NO_3]$ in the solid state are adopted in solution.

Chelation of rigid 1,10-phenanthroline ligands in solution is ensured from a stability constant study[11] of $[MeHg(1,10\text{-phen})]^+$ since this ligand cannot act as a unidentate, but for the 2,2'-bipyridyl ligands chelation needs to be established spectroscopically before interpretation of NMR data in terms of bonding is permissible.

Except for $[MeHg(3,3'\text{-dmbpy})][NO_3]$ coupling constants $J(^1H\text{–}^{199}Hg)$ for the methylmercury group are similar in complexes of the 2,2'-bipyridyl and 1,10-phenanthroline ligands (235.1–239.8 Hz) and are higher than in the pyridine complexes (225.2–229.6 Hz) (Table II). The higher values are assumed to indicate chelation, and, consistent with this interpretation, the ligand 3,3'-dmbpy, which cannot act as a chelate, forms a complex with a value of $J(^1H\text{–}^{199}Hg)$ (230.4 Hz) similar to the complexes of unidentate ligands as expected for structure I. In addition, when $J(^1H\text{–}^{199}Hg)$ is plotted against $\log K_H$ for the ligands (Figure 3), the value for this complex (12) is close to the line (least-squares fit) passing through values for the unidentate pyridines (1–7). This complex and $[MeHg(2\text{-Bzlpy})][NO_3]$ are the only ones that show an upfield shift of the methylmercury resonance from the value of methylmercuric nitrate, consistent with the presence of a nonbonded aromatic ring having a shielding effect resulting from a different orientation (I) than expected in complexes with chelate ligands (Figure 1).[29] Since 3,3'-

Table II. NMR Data for the Complexes[a]

	^{13}C	^{1}H NMR								
Complex	NMR Me_{Hg}[b]	Me_{Hg}[c]	$\lvert J(^1H-^{199}Hg)\rvert$[d]	Ligand protons[c,e,f]						Coupl const within ligand[f]
$MeHgNO_3$	−72.5	−2.597	251.8							
A. Pyridine, 2,2'-Bipyridyl, and Related Complexes										
				H_2	H_3	H_4	H_5	H_6	Me	
[MeHg(py)][NO_3]	−71.3	−2.564	229.6[g]	5.06 m	4.24 m	4.61 t	4.24 m	5.06 m		$J_{3,4} \equiv J_{4,5} = 7.6$
[MeHg(2-mpy)][NO_3]	−69.9	−2.533	227.9		4.10 d	4.50 m	4.06 m	5.00 d	−0.78	$J_{3,4} = 7.7; J_{5,6} = 5.5$
[MeHg(3-mpy)][NO_3]	−71.3	−2.589	228.2	4.91 m		4.44 d	4.12 m	4.89 m	−1.16	$J_{4,5} = 7.8$
[MeHg(4-mpy)][NO_3]	−71.2	−2.585	227.5	4.89 d	4.05 d		4.05 d	4.89 d	−1.12	$J_{2,3} \equiv J_{5,6} = 5.8$
[MeHg(2,4-dmpy)]NO_3	−69.9	−2.559	225.7		3.93		3.90 d	4.83 d	−0.85 (2) −1.17 (4)	$J_{5,6} = 6.0$
[MeHg(2,6-dmpy)][NO_3]	−68.3	−2.680	225.2		3.92 d	4.39 t	3.92 d		−0.80	$J_{3,4} = 7.8$
[MeHg(2-Bzlpy)][NO_3][h]	−70.3	−2.850	229.6		*h*	4.56 m	*h*	5.01 dd		$J_{4,3} = J_{4,5} = 7.7; J_{5,6} = 5.3; J_{4,6} = 1.5$
[MeHg(bpy)][NO_3]	−72.9	−2.499	238.8		4.99 d	4.66 td	4.24 td	5.18 d		$J_{3,4} = 8.0; J_{4,5} = 7.7; J_{5,6} = 4.9; J_{3,5} = 1.2; J_{4,6} = 1.7$
[MeHg(6,6'-dmbpy)][NO_3]·H_2O	−70.2	−2.508	235.9		4.79 d	4.52 t	4.08 d		−0.75	$J_{3,4} = 7.9; J_{4,5} = 7.8$
[MeHg(5,5'-dmbpy)][NO_3]	−73.0	−2.518	237.0		4.79 d	4.43 d		4.97	−1.13	$J_{3,4} = 7.0$
[MeHg(4,4'-dmbpy)][NO_3]	−73.1	−2.550	235.1		4.75		3.97 d	4.92 d	−1.08	$J_{5,6} = 5.1$
[MeHg(3,3'-dmbpy)][NO_3]	−71.6	−2.893	230.4			4.48 d	4.11 dd	5.04 d	−1.40	$J_{4,5} = 7.9; J_{5,6} = 5.0$
$MeHgNO_3\cdot{}^1/_2$(3,3'-dmbpy)		−2.776	240.5			4.56 d	4.21 dd	5.11 d	−1.38	$J_{4,5} = 7.8; J_{5,6} = 5.1$
B. 1,10-phenanthroline and Related Complexes										
				$H_{2,9}$	$H_{3,8}$	$H_{4,7}$	$H_{5,6}$	Me		
[MeHg(phen)][NO_3]	−72.8	−2.383	239.8	5.53 dd	4.53 m	5.19 dd	4.60 m			$J_{2,3} = 4.7; J_{2,4} = 1.4; J_{3,4} = 5.8$
[MeHg(2,9-dmphen)][NO_3]·H_2O	−70.3	−2.384	236.0		4.34 d	5.02 d	4.42	−0.56		$J_{3,4} = 8.3$
[MeHg(4,7-dmphen)][NO_3][i]		−2.416	236.8	5.32 d	4.36 dd		4.74	−0.69		$J_{2,3} = 5.0; J_{3,4} = 0.6$
[MeHg(5,6-dmphen)][NO_3][i]		−2.396	238.0	5.44 dd	4.54 dd	5.38 dd		−0.79		$J_{2,3} = 4.8; J_{2,4} = 1.1; J_{3,4} = 8.7$

[a] Solutions 0.1 *M* in CD_3OD. Atom-numbering schemes for 2,2'-bipyridyls and 1,10-phenanthrolines are shown in Figure 1 and structure II, and for 2,2'-bipyridyls *n* and *n'* protons are equivalent. Abbreviations for ligands are given with Table I. [b] Chemical shift from internal 1,4-dioxane; accuracy to ca. ±0.1 ppm. [c] Chemical shift from internal 1,4-dioxane; accuracy to ca. 0.005 ppm. [d] Accuracy to ca. ±0.5 Hz. The sign of the coupling constant is assumed to be negative.[17,18] [e] Mean values. Key: m, multiplet; d, doublet; dd, doublet of doublets; td, triplet of doublets; vb, very broad. [f] First-order analysis.[19] For 1,10-phenanthrolines $J_{xy} \equiv J_{11-x,11-y}$. [g] Literature values 226.0 (0.2 *M* in D_2O),[14] 227 (5 mol % in pyridine or D_2O).[20] [h] Methylene resonance 0.83 ppm (vb); broad multiplet at 3.4–4.25 ppm includes H_3, H_5, and phenyl group resonances. [i] Insufficiently soluble for ^{13}C NMR spectroscopy. ^{1}H NMR spectra measured in pulsed Fourier transform mode.

dmbpy acts as a unidentate in solution, we attempted to prepare a complex with this ligand acting as a bridge between two methylmercury groups. A solid of composition $MeHgNO_3\cdot{}^1/_2$(3,3'-dmbpy) was isolated, but when this compound is in solution, $J(^1H-^{199}Hg)$ is close to the value expected for an equimolar mixture of [MeHg(3,3'-dmbpy)][NO_3] and $MeHgNO_3$ [calcd (251.8 + 230.4)/2 = 241.1 Hz; found 240.5 Hz].

Additional evidence for chelation comes from analysis of the chemical shifts of the $H_{3,3'}$ and $H_{5,5'}$ protons of the 2,-2'-bipyridyl, 6,6'-dimethyl-2,2'-bipyridyl, and 4,4'-dimethyl-2,2'-bipyridyl complexes using the approach of Spotswood et al.,[35-37] who correlated interplanar angles in 2,2'-bipyridyls and bridged biquaternary 2,2'-bipyridyls with the relative positions of these resonances. $H_{5,5'}$ protons lie on the C_5–C_2–$C_{2'}$–$C_{5'}$ rotational axis (Figure 1) and serve as a useful internal reference for the variation in chemical shift of $H_{3,3'}$ protons which are also β to the nitrogen atoms. They showed that as the interplanar angle between the two rings is increased from 0° (coplanar), the chemical shift difference between $H_{3,3'}$ and $H_{5,5'}$ decreases.[38] Possible interplanar angles in methylmercury complexes are restricted to the range 0° (cis bidentate, Figure 1) to ca. 90° (unidentate, I), as conformations approaching that of the free ligands (trans coplanar established for 2,2'-bipyridyl and 4,4'-dimethyl-2,2'-bipyridyl in methanol[37]) involve excessive steric interaction between $H_{3'}$ and the methylmercury group. The chemical shift differences between $H_{3,3'}$ and $H_{5,5'}$ in complexes of 2,2'-bipyridyl, 6,6'-dimethyl-2,2'-bipyridyl, and 4,4'-dimethyl-2,2'-bipyridyl are 0.75, 0.71, and 0.71 ppm, respectively (Table I). These values are appropriate for the cis bidentate conformation and are similar to values in other complexes where bidentate coordination is ensured, e.g., PtX_2L (X = Cl, L = 2,2'-bipyridyl, 0.62 ppm; X = Cl, L = 4,4'-dimethyl-2,2'-bipyridyl, 0.62 ppm).[39] A detailed account of the application of ^{1}H and ^{13}C NMR spectroscopy to determination of conformation of coordinated 2,2'-bipyridyls in these and related complexes will be presented elsewhere.[40]

Discussion

With chelation of 2,2'-bipyridyl and 1,10-phenanthroline ligands established in solutions of the complexes NMR data may be interpreted in terms of bonding involving three-coordinate mercury.

A number of studies have shown that values of $J(^1H-^{199}Hg)$ for a large range of MeHgX compounds, e.g., Me_2Hg (104.3 Hz) and MeHgCl (215.2 Hz) in pyridine,[20] correlate with the stability constants for formation of MeHgX,[41-43] pK_a of HX,[42-47] and electronegativity of X.[20,47] These observations have been explained by assuming that the relative magnitude of the coupling constant is due mainly to the Fermi contact interaction, specified by the s-electron density on the coupled nuclei and carbon.[20,47] An increase in electronegativity of X in MeHgX is expected to increase the s character of the hybrid orbital of mercury involved in bonding to carbon[18,20,47] and to increase the effective nuclear charge for the mercury 6s orbital resulting in a contraction of that orbital.[18,20] These effects are consistent with the increase in coupling constant

Table III. Selected Structural Data for $[MeHg(2,2'\text{-bpy})][NO_3]$ and Methylmercury-Amino Acid Complexes

Complex	Coord no.[a]	C-Hg-N, deg	Hg-C, Å	Hg-N, Å	Hg-N'(O), Å
$[MeHg(2,2'\text{-bpy})][NO_3]$[b]	3	164.0 (18)	2.066 (58)	2.236 (38)	2.421 (32)
$MeHgNH_2CH(CO_2)CMe_2SHgMe$[c]	3	168.1	2.165 (6)	2.216 (5)	2.708 (4)
$MeHgNH_2CH(CO_2)CH_2CH_2SMe$[d]	4	173 (2)	2.11 (5)	2.06 (4)	2.67 (3), 2.72 (3)

[a] Including all atoms at less than sum of van der Waals radii. [b] From ref 8. [c] From ref 3. Data for amine-bonded mercury. [d] From ref 4.

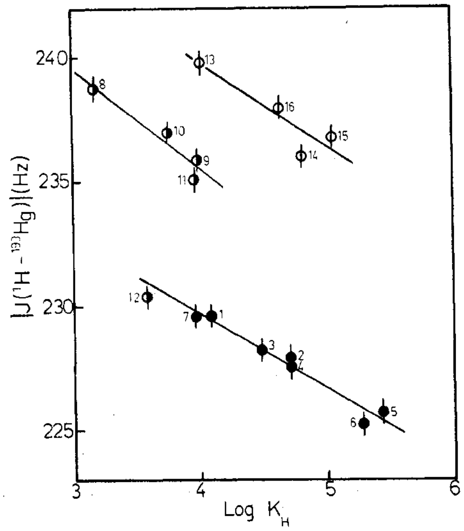

Figure 3. $|J(^1H-^{199}Hg)|$ for $[MeHgL][NO_3]$ (0.1 *M* in CD_3OD) vs. log K_H for the ligands (L). log K_H values are those obtained for a 50% dioxane–water mixture as solvent: (⧫) L = pyridines; (ϕ) L = 2,2'-bipyridyls; (ϕ) L = 1,10-phenanthrolines. Ligands with log K_H values in parentheses are (1) py (4.09), (2) 2-mpy (4.71), (3) 3-mpy (4.49), (4) 4-mpy (4.72, lit.[30] 5.11 ± 0.03), (5) 2,4-dmpy (5.44), (6) 2,6-dmpy (5.28), (7) 2-Bzlpy (3.97), (8) bpy (3.18, lit.[31,32] 3.62 ± 0.02), (9) 6,6'-dmbpy (3.99, lit.[31,32] 4.23 ± 0.02), (10) 5,5'-dmbpy (3.76, lit.[31,32] 3.97 ± 0.03), (11) 4,4'-dmbpy (3.97, lit.[31,32] 4.40 ± 0.03), (12) 3,3'-dmbpy (3.59), (13) phen (4.03, lit.[32] 4.53 ± 0.03), (14) 2,9-dmphen (4.82, lit.[33] 5.42), (15) 4,7-dmphen (5.06, lit.[31,32] 5.40 ± 0.02), and (16) 5,6-dmphen (4.65, lit.[31,32] 5.00 ± 0.03). Abbreviations for ligands are given with Table I. Least-squares lines have the following correlation coefficients: (⧫) −0.98, (ϕ) excluding 3,3'-dmbipy (12) −0.96, (ϕ) −0.90. Similar lines are obtained using (i) literature values of log K_H (50% dioxane–water) for ligands 8–11 (2,2'-bipyridyls, correlation coefficient −1.0) and 13–16 (1,10-phenanthrolines, correlation coefficient −0.98) with lines translated ca. 0.36 log K_H unit higher and (ii) literature values of log K_H (aqueous solutions) for ligands 1–7 (pyridines,[31,34] correlation coefficient −0.97) and 13–16 (phenanthrolines,[31] correlation coefficient −0.95) with lines translated ca. 0.85 and 1.4 log K_H units higher, respectively.

observed with increasing electronegativity of X. Although the Fermi contact mechanism as the sole major contributor to the magnitude of heavy metal–proton spin–spin coupling constants has been questioned,[48] a recent semiempirical molecular orbital study of $J(^1H-^{199}Hg)$ has provided additional support for it, with calculations showing that orbital contraction of the 6s orbital of mercury with increasing electronegativity of X is an important factor.[18] Hybridization involving 6s and 6p orbitals only is considered since experimental evidence[49] and a theoretical study[18] indicate that d_{z^2}–s hybridization[50] is not significant in (linear) methylmercury compounds.

We find that values of $J(^1H-^{199}Hg)$ for $[MeHgL][NO_3]$ correlate with protonation constants of neutral ligands, log K_H (i.e., pK_a of LH^+), in a manner similar to that reported for MeHgX [$J(^1H-^{199}Hg)$ decreasing with increasing pK_a of HX[42–47]] for both two- and three-coordinate mercury (Figure 3).[51] Perhaps the most striking observation on increase in coordination number from 2 (pyridines) to 3 (2,2'-bipyridyls and 1,10-phenanthrolines) is the very small increase in $J(^1H-^{199}Hg)$ (4.7–14.6 Hz) compared with the wide range (ca. 160 Hz) spanned by linear sp-hybridized methylmercury compounds. A similar increase in $J(^1H-^{199}Hg)$ has been observed on weak solvation of methylmercury compounds by polar solvents (maximum increase ca. 11 Hz)[2,5,6] and on formation of $[MeHg(SCN)_3]^{2-}$ from MeHgSCN in aqueous solution (6.9 Hz).[52,53] The small increase in coupling constant presumably indicates only a slight alteration in s-electron density of the hybrid orbital of mercury bonding to carbon and/or a slight alteration of effective charge on the mercury and carbon atoms with consequent contraction or expansion of the valence s orbitals. An sp^2 hybridization scheme for the three-coordinate complexes would lower the s-electron density in the mercury–carbon bond from that in the linear complexes and thus lower $J(^1H-^{199}Hg)$. Small upfield shifts of ^{13}C resonances of the methylmercury group on increase in coordination number are assumed to indicate only minor changes in effective charge on mercury and carbon (chemical shifts upfield from 1,4-dioxane are 70.5 ± 2.2 ppm for complexes of unidentate ligands, 72.3 ± 2.1 ppm for complexes of bidentate 2,2'-bipyridyls, and 71.6 ± 1.3 ppm for complexes of phen and 2,9-dmphen, Table II). The mercury–carbon coupling constant, $J(^{13}C-^{199}Hg)$, for the complexes is expected to be more sensitive than $J(^1H-^{199}Hg)$ to changes in mercury–carbon bonding. Attempts to measure $J(^{13}C-^{199}Hg)$ were unsuccessful.[54]

With NMR data indicating only slight changes in mercury–carbon bonding on increase in coordination number of mercury it is apparent that mercury–carbon bonding is the dominant bonding requirement and that an sp hybridization scheme similar to that in complexes of the pyridine ligands may be a suitable bonding model for the three-coordinate complexes involving 2,2'-bipyridyls and 1,10-phenanthrolines. A bonding scheme with sp hybridization is also consistent with mercury–nitrogen bond lengths and their angular relationship to the sp hybridization axis (Hg–C) (Figure 2). The nitrogen atom (N) forming the largest angle with the methylmercury group [164.0 (18)° vs. 126.0 (17)° for N'] is better placed to allow overlap of its lone pair with an sp hybrid orbital of mercury, and thus the Hg–N bond is shorter than Hg–N'.[55] With an sp hybridization scheme for the dominant C–Hg–N group another possible bonding mode of N' to mercury is via overlap of the nitrogen lone pair with a vacant 6p orbital of mercury.

It is of interest to compare the structure of $[MeHg(2,2'\text{-bpy})][NO_3]$ with those of amino acid complexes, as these are the only structures reported that contain methylmercury bonded to a neutral nitrogen donor. Data in Table III show that there is little alteration in Hg–C bond lengths as the C–Hg–N angle deviates further from linearity but that Hg–N lengthens by ca. 0.2 Å. These trends are consistent with the above discussion of a dominant Hg–C bonding requirement and of bond lengths and angles assuming sp hybridization for mercury.

We conclude that mercury–carbon bonding in $[MeHgL][NO_3]$ (L = 2,2'-bipyridyls, 1,10-phenanthrolines) complexes with three-coordinate mercury is similar to that in $[MeHgL][NO_3]$ (L = pyridines) with linear geometry for mercury and that an sp hybridization bonding model accounts for both the NMR spectra of these complexes and the coordination geometry of the 2,2'-bipyridyl complex. It is considered that solid amino acid complexes of methylmercury have similar bonding.

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Registry No. [MeHg(py)][NO$_3$], 35917-32-9; [MeHg(2-mpy)][NO$_3$], 56665-03-3; [MeHg(3-mpy)][NO$_3$], 56665-05-5; [MeHg(4-mpy)][NO$_3$], 56665-01-1; [MeHg(2,4-dmpy)][NO$_3$], 57527-21-6; [MeHg(2,6-dmpy)][NO$_3$], 57527-23-8; [MeHg(2-Bzlpy)][NO$_3$], 57527-25-0; [MeHg(bpy)][NO$_3$], 56665-11-3; [MeHg(6,6'-dmbpy)][NO$_3$], 56665-13-5; [MeHg(5,5'-dmbpy)][NO$_3$], 56704-80-4; [MeHg(4,4'-dmbpy)][NO$_3$], 56704-82-6; [MeHg(3,-3'-dmbpy)][NO$_3$], 56704-78-0; MeHgNO$_3\cdot{}^1/_2$(3,3'-dmbpy), 57527-27-2; [MeHg(phen)][NO$_3$], 56704-76-8; [MeHg(2,9-dmphen)][NO$_3$], 56704-74-6; [MeHg(4,7-dmphen)][NO$_3$], 57527-29-4; [MeHg(5,6-dmphen)][NO$_3$], 57527-32-9.

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(29) A similar upfield shift resulting from a phenyl group has been noted[7] for the phenylalanine complex MeHg$^+$–NH$_2$CH(CO$_2^-$)(CH$_2$Ph) which has a methylmercury resonance 0.5 ppm upfield from that of the glycine complex MeHg$^+$–NH$_2$CH$_2$CO$_2^-$.

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(55) An alternative sp^2 hybridization model is expected to have stronger Hg–N' bonding as the C–Hg–N' angle is close to that expected for trigonal geometry [126.0 (17)° vs. 120°].