

spectra of our compounds suggests that the two amine nitrogen atoms at 2.50 Å from Cu have a much larger effect on the energy of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition than a single nitrogen atom on the axial position of a square pyramid does.^{32a} In fact, the spectrum of our compound is comparable to that of square-pyramidal structures with one axial ligand at about 2.15 Å from the copper atom.^{27b,35}

Concluding Remarks. The ligand EDTB is capable of forming copper coordination compounds with unusual geometries. When two Cu(II) ions per ligand are present, different coordination geometries are assumed, depending on the anion. In view of the crystal structure and of the electronic and ESR spectra, the copper coordination in the $\text{Cu}(\text{EDTB})^{2+}$ cation has to be described as highly distorted square pyramidal.

Copper derivatives of EDTB ligands with methyl substituents on benzimidazole carbon or nitrogen atoms are under investigation, and related ligand systems in which sulfur donor

atoms are present have been synthesized.³⁶

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Registry No. $\text{Cu}(\text{EDTB})(\text{BF}_4)(\text{BF}_3\text{OC}_2\text{H}_5)\cdot\text{H}_2\text{O}$, 77590-35-3; $\text{Cu}(\text{EDTB})\text{Cl}_2$, 77590-36-4; $\text{Cu}(\text{EDTB})\text{Br}_2$, 77590-37-5; $\text{Cu}(\text{EDTB})(\text{NO}_3)_2$, 77590-38-6; $\text{Cu}(\text{EDTB})(\text{ClO}_4)_2$, 77590-39-7; $\text{Cu}(\text{EDTB})(\text{BF}_4)_2$, 72555-19-2; $\text{Cu}_2(\text{EDTB})\text{Cl}_4\cdot 2\text{H}_2\text{O}$, 77630-27-4; $\text{Cu}_2(\text{EDTB})\text{Br}_4\cdot 2\text{H}_2\text{O}$, 72555-16-9; Cu , 7440-50-8; $\text{Cu}_2(\text{EDTB})(\text{ClO}_4)_4\cdot 2\text{H}_2\text{O}$, 77590-41-1; $\text{Cu}_2(\text{EDTB})(\text{BF}_4)_2$, 77590-43-3; $\text{Cu}_2(\text{EDTB})(\text{ClO}_4)_2$, 77590-44-4; EDTB, 72583-85-8.

Supplementary Material Available: Calculated positional parameters (Table III) for the hydrogen atoms and a listing of structure factor amplitudes (Table IV) (5 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of Methylmercury(II). Synthesis, ¹H NMR, and Crystallographic Studies of Cationic Complexes of MeHg^{II} with Ambidentate and Polydentate Ligands Containing Pyridyl and N-Substituted Imidazolyl Donors and Involving Unusual Coordination Geometries¹

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Complexes $[\text{MeHgL}]\text{NO}_3$ (L = 4,4',4''-triethyl-2,2':6',2''-terpyridyl (Et_3terpy), terpy, bis(2-pyridyl)methanes ((py)₂CH₂'s), (py)₂CMe₂, (py)₂CET₂, tris(2-pyridyl)methane, several N-alkylimidazoles, N-(2-pyridyl)imidazole, and N-methyl-2-(2-pyridyl)imidazoles) are obtained from addition reactions in acetone. Proton magnetic resonance spectroscopy is used to deduce coordination behavior of potential uni- or polydentate ligands in methanol, indicating that Et_3terpy , terpy, (py)₂CH₂'s, and N-methyl-2-(2-pyridyl)imidazoles act as bidentates to give three-coordinate mercury, but (py)₂CR₂ (R = Me, Et) are present as unidentates. A linear relation is obtained between $^2J(^1\text{H}-^{199}\text{Hg})$ for $[\text{MeHgL}]^+$ and protonation constants for L, where L = N-alkylimidazoles, and the relation is similar to that obtained previously for L = pyridines. The ambidentate ligand N-(2-pyridyl)imidazole binds to mercury via the imidazole ring. Crystalline $[\text{MeHg}((\text{py})_2\text{CH}_2)]\text{NO}_3$ has (py)₂CH₂ present as a bidentate ligand with "T-shape" coordination geometry based on a dominant C-Hg-N moiety [Hg-N = 2.16 (1) Å, C-Hg-N = 172 (1)°] and a weaker Hg-N' bond [2.75 (2) Å]. [Crystal data: space group $P2_1/n$, Z = 4, a = 16.875 (2) Å, b = 8.540 (1) Å, c = 9.353 (1) Å, β = 96.544 (8)°, R = 0.054 for 1142 reflections having $I \geq 3\sigma(I)$.] Crystalline $[\text{MeHg}(\text{Et}_3\text{terpy})]\text{NO}_3$ has Et_3terpy present as a tridentate ligand with MeHg^{II} bonded strongly to the central nitrogen [2.26 (2) Å, C-Hg-N = 171 (1)°] and weakly to the terminal nitrogens [2.51 (2), 2.61 (2) Å]. [Crystal data: space group $P2_1/n$, Z = 4, a = 9.115 (2) Å, b = 15.725 (3) Å, c = 15.566 (3) Å, β = 94.465 (14)°, R = 0.063 for 1286 observed intensities having $I \geq 3\sigma(I)$.] Syntheses of new ligands containing pyridyl and N-methylimidazolyl donor groups are described.

The MeHg^{II} cation is the fundamental organomercury species, and with a coordination geometry restricted almost entirely to linear geometry,^{4,5} e.g., MeHgX (X = halide) and $[\text{MeHg}(\text{py})]^+$, may be regarded as one of the simplest Lewis acids, and as such it has been studied extensively as a prototype soft acid,⁶ as a model spectroscopic probe for binding of metal

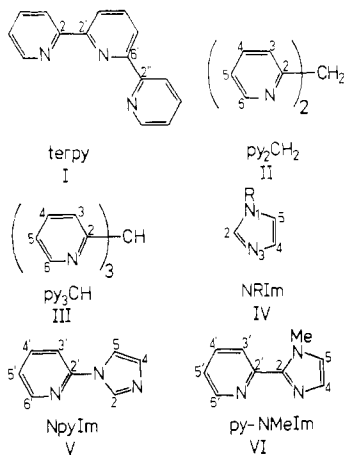
ions to complex molecules,⁷ and finds application as a probe for the study of polynucleotides^{5,8} and proteins.⁵ However, 2,2'-bipyridyls act as bidentates toward MeHg^{II} in $[\text{MeHgL}]\text{NO}_3$ ^{9,10} to give irregular three-coordinate for mercury based on a dominant C-Hg-N moiety [164 (1)°, Hg-N = 2.24 (3) Å] and a weaker Hg-N' bond [2.43 (3) Å]¹⁰ with both bonds longer than the value for linear $[\text{MeHg}(\text{py})]^+$

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[2.12 (2) Å]¹¹ but much shorter than the sum of van der Waals radii (3.23 Å).¹²

In studying complexes of pyridines and 2,2'-bipyridyls, we have developed a ¹H NMR method which may be generally applicable for determination of the state of coordination of potential polydentate ligands containing pyridyl donor groups.^{9,14} We report here results of an attempt to exploit this approach with a series of ligands (I–VI, including sub-



stituted derivatives) chosen with a view to (1) allow MeHg^{II} to assume the normal linear geometry or higher coordination numbers by use of nonrigid polydentates, (2) present MeHg^{II} with donor set geometries different from 2,2'-bipyridyls, e.g., potential planar (I) and tripodal (III) tridentates, (3) use ligands without resonance stabilization between rings (II, III) that may favor chelate behavior by 2,2'-bipyridyls, and (4) study *N*-alkylimidazoles (IV) to establish a ²J(¹H–¹⁹⁹Hg), log *K*_H correlation for ligands of higher basicity than pyridines and to determine whether the mode of action of ambidentate (V) and potential bidentate (VI) ligands containing both pyridyl and imidazolyl donor groups can be ascertained.

Choice of these ligands has necessitated improvement of earlier synthetic routes, in addition to synthesis of some new ligands, and as they are of potential use in coordination chemistry generally, their synthesis is presented in detail.

Experimental Section

Preparation of Ligands. Commercially available ligands were recrystallized or distilled: 2,2':6',2''-terpyridyl [Fluka, petrol (40–60 °C)], *N*-benzylimidazole and 1,2-dimethylimidazole (Ega-Chemie, diethyl ether), 1,2,4,5-tetramethylimidazole (Ega-Chemie, petrol), 1-methylimidazole [Ega-Chemie, distilled]. The ligands *N*-methyl-2-phenylimidazole¹⁵ [bp 120 °C (0.3 mm)], *N*-(2-pyridyl)-imidazole [mp 39.5–42 °C (lit.¹⁶ mp 38–40 °C)], 2-(2-pyridyl)-imidazole [mp 134–135 °C (lit.¹⁷ mp 134–135 °C)], 2-(6-methyl-2-pyridyl)imidazole [mp 170 °C (lit.¹⁷ mp 170 °C)], 4,4'-diethyl-2,2'-bipyridyl [bp 195 °C (ca. 30 mm) [lit.¹⁸ bp 210 °C (30 mm)]]

and 4,4',4''-triethyl-2,2':6',2''-terpyridyl [mp 90° (lit.¹⁹ mp 89–91 °C)] were prepared as described.^{16,17,19}

The bis(2-pyridyl)methanes were prepared by methods similar to those reported for (py)₂CH₂ and (py)₂CHEt;²⁰ the new ligands (py)₂CR₂ (R = Me, Et) and (py)₂CMe₂Ph were prepared from (py)₂CH₂ via (py)₂CHR, and from (py)CH₂Ph via (py)CH(Me)Ph, respectively; tris(2-pyridyl)methane was more conveniently prepared from (py)₂CH₂ than the reported²¹ method. The ligand (6-methyl-2-pyridyl)(2-pyridyl)methane (6-MepyCH₂(py)) was prepared by a route similar to that for (py)₂CH₂, rather than the reported²² method. Full details of the preparation of 6-MepyCH₂(py) is given as an example, followed by appropriate comments for the other ligands. As the melting point of *N*-methyl-(2-pyridyl)imidazole is quite different from the reported value its preparation is given in detail; the new ligand *N*-methyl-2-(6-methyl-2-pyridyl)imidazole was prepared similarly. Reactions were carried out in a nitrogen atmosphere; reagents were purified by storage over type 4A molecular sieves (iodomethane, pyridine-2-carboxaldehyde), distillation under reduced pressure (6-methylpyridine-2-carboxaldehyde), distillation and storage over molecular sieves (bromobenzene, 2-benzylpyridine, 2-bromopyridine, bromoethane, dimethyl sulfate, petroleum), distillation and storage over sodium (benzene, toluene), distillation followed by percolation (1 L/h) through a column (1 m) of molecular sieves (ethanol, methanol), distillation from KOH followed by column treatment and storage over molecular sieves (2-picoline, pyridine), or drying over CaCl₂ followed by distillation, column treatment, and storage over sodium (diethyl ether), where all distillations involved use of a fractionating column. Melting points are uncorrected. In addition to elemental analysis (C, H, N) for new ligands, all ligands were characterized by preparation of MeHg^{II} derivatives.

(6-Methyl-2-pyridyl)(2-pyridyl)methane. 2-Picoline (20 mL, 0.2 mol) in diethyl ether (25 mL) was added slowly with stirring to a solution of phenyllithium (0.2 mol) in diethyl ether (100 mL) at 0 °C. After the solution of 2-picolylithium was stirred for 30 min, 2-picoline (20 mL) was added slowly. Benzene or toluene (100 mL) was added and diethyl ether removed by distillation. The remaining solution was refluxed (18 h) and cooled to ca. 40 °C, and water (100–150 mL) was added cautiously with stirring. The solution was shaken vigorously and the benzene layer separated and dried over K₂CO₃. The suspension was filtered, and the solvent and any remaining 2-picoline were removed as completely as possible by rotary evaporation under reduced pressure. The residual oil was distilled with use of a fractionating column, and the fraction boiling at 80–130 °C (0.1–0.5 mm) was collected. Hydrochloric acid (12 M, 42 mL) was added to the crude 6-MepyCH₂(py), followed by water (100 mL), and diethyl ether was added to extract water insoluble impurities. The aqueous layer was separated and reduced to low volume (ca. 50 mL) under reduced pressure and hot ethanol added. Crystals were collected and recrystallized from ethanol. The salt was dissolved in a small quantity of water in a separating funnel and K₂CO₃ solution added until effervescence ceased; the required product was extracted with chloroform, the solution dried over K₂CO₃ and filtered, and chloroform removed under reduced pressure to obtain a colorless oil (7.36 g, 20%).

Bis(2-pyridyl)diethylmethane ((py)₂C(Et)₂). The monoethyl derivative, (py)₂C(Et)H, was prepared as described²⁰ [bp 125 °C (0.2 mm) [lit.²⁰ bp 125 °C (0.2 mm)]], and the same method was followed to prepare (py)₂C(Et)₂ from (py)₂C(Et)H. The residual oil (6.5 g) was distilled [130 °C (0.6 mm)], concentrated HCl (10 mL) added, the solution taken to dryness by rotary evaporation, and the residue dissolved in hot ethanol (75 mL). On addition of diethyl ether (75 mL) the white salt which formed was collected and converted by neutralization to the required product, a colorless oil which formed crystals on cooling [5.6 g (71% from (py)₂CH₂), mp 51–53 °C]. Anal. Calcd for C₁₅H₁₈N₂: C, 79.6; H, 8.0; N, 12.4. Found: C, 79.6; H, 7.8; N, 12.3.

Bis(2-pyridyl)dimethylmethane ((py)₂CMe₂). was prepared similarly, with use of iodomethane [70% from (py)₂CH₂, mp 48.5–50.5 °C]. Anal. Calcd for C₁₃H₁₄N₂: C, 78.7; H, 7.1; N, 14.1. Found: C, 78.7; H, 7.0; N, 14.1.

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- (12) For N, 1.5 Å¹³; for Hg, 1.5⁴ or 3.23 Å (using Grdenić's⁴ upper limit of 1.73 Å for the radius of mercury). Recent structural determinations, e.g., close contacts between mercury atoms of 3.48 (1)–3.51 (1) [R. M. Barr, M. Goldstein, T. N. D. Hairs, M. McPartlin, and A. J. Markwell, *J. Chem. Soc., Chem. Commun.*, 221 (1974)] and 3.407 (2) Å [A. J. Canty, M. Fyfe, and B. M. Gatehouse, *Inorg. Chem.*, **17**, 1467 (1978)] lend support to the upper limit of 1.73 Å suggested by Grdenić. This has been suggested as a general value for the van der Waals radius of mercury, although some interactions at distances corresponding to a larger radius cannot be excluded [A. J. Canty and G. B. Deacon, *Inorg. Chim. Acta*, **45**, L225 (1980)].
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Table I. Characterization Data for [MeHgL]NO₃

complex	% calcd			% found			$\nu(\text{Hg-C}),$ cm ⁻¹	$\delta(\text{MeHg})^{\text{a-c}}$	$^1J(^1\text{H}-^{199}\text{Hg})_1^{\text{a,d}}$ Hz
	C	H	Hg	C	H	Hg			
[MeHg(4,4'-Et ₂ (bpy))]NO ₃ ^e	36.8	3.9	40.9	36.7	3.9	41.0	552	-2.52	236.0
[MeHg(terpy)]NO ₃	37.6	2.8	39.3	38.0	3.0	39.5	526	-2.86	243.0
[MeHg(Et ₃ terpy)]NO ₃ ^f	44.4	4.4	33.7	44.7	4.61	33.7		-2.94	243.1
[MeHg((py) ₂ CH ₂)]NO ₃ ^g	32.2	2.9	44.8	32.2	3.0	44.9	552, 522 ^l	-2.49	235.4
[MeHg(6-MepyCH ₂ (py))]NO ₃ ^h	33.8	3.3	43.4	33.6	3.1	43.2	<i>m</i>	-2.48	232.2
[MeHg((py) ₂ CMe ₂)]NO ₃	35.3	3.6	42.1	35.2	3.7	42.2	549 ⁿ	-2.85	234.7
[MeHg((py) ₂ CEt ₂)]NO ₃	38.1	4.2	39.8	38.6	4.3	40.0	555	-2.93	232.5
[MeHg((py) ₃ CH)]NO ₃	38.9	3.1	38.2	39.0	3.3	37.7	527	-2.43	243.1
[MeHg(<i>N</i> -MeIm)]NO ₃	16.7	2.5	55.8	16.6	2.5	55.6	570	-2.66	219.5 ^o
[MeHg(2-Me- <i>N</i> -MeIm)]NO ₃ ⁱ	19.3	3.0	53.7	19.3	3.0	53.6	559	-2.66	217.1
[MeHg(Me ₃ - <i>N</i> -MeIm)]NO ₃	23.9	3.8	49.9	23.9	3.7	49.7	<i>n</i>	-2.61	213.6
[MeHg(2-Ph- <i>N</i> -MeIm)]NO ₃	30.3	3.0	46.0	30.2	3.1	46.6	563	-2.80	219.8
[MeHg(<i>N</i> -BzIm)]NO ₃ ^j	30.3	3.0	46.0	30.1	3.0	46.3	559	-2.67	220.6
[MeHg(py- <i>N</i> -MeIm)]NO ₃	27.5	2.8	45.9	27.6	2.8	46.2	556	-2.61	224.7
[MeHg(6-Mepy- <i>N</i> -MeIm)]NO ₃ ^k	29.3	3.1	44.5	29.2	3.3	44.8	<i>m</i>	-2.61	224.0
[MeHg(<i>N</i> -pyIm)]NO ₃	25.6	2.4	47.4	26.0	2.3	47.0	563	-2.62	224.2
MeHgNO ₃ + (py)CMe ₂ Ph								-3.10	235.0

^a Solutions ca. 0.1 M in CD₃OD. ^b Chemical shifts from internal 1,4-dioxane; accuracy to about 0.005 ppm. ^c For complexes of pyridines, except for 2-Bz(py) (-2.85 ppm)⁹ and (py)CMe₂Ph, $\delta(\text{Me-Hg}) = -2.47$ to -2.68 ,⁹⁻¹⁴ for bidentate 2,2'-bipyridyls $\delta(\text{Me-Hg}) = -2.499$ to -2.550 ,⁹ and for 3,3'-dmbpy $\delta(\text{Me-Hg}) = -2.893$.⁹ ^d Accuracy to ca. ± 0.5 Hz. The sign of the coupling constant is assumed to be negative.²⁴ ^e 4,4'-Et₂(bpy) = 4,4'-diethyl-2,2'-bipyridyl. ^f Et₃terpy = 4,4',4''-triethyl-2,2':6',2''-terpyridyl. ^g (py)₂CH₂ = dipyrindylmethane. ^h 6-MepyCH₂(py) = (6-methyl-2-pyridyl)(2-pyridyl)methane. ⁱ 2-Me-*N*-MeIm = 1,2-dimethylimidazole. ^j *N*-BzIm = *N*-benzylimidazole. ^k 6-Mepy-*N*-MeIm = *N*-methyl-2-(6-methyl-2-pyridyl)imidazole. Other ligands similarly abbreviated. ^l Assignment is uncertain: one of these may be a ligand absorption. ^m The ligand has several bands in the region 500-600 cm⁻¹; thus assignment is not possible. ⁿ The ligand has a band in this region; thus this band may cover a coincident or nearby $\nu(\text{Hg-C})$ absorption. ^o Literature value 218.8 (in D₂O).⁵

2-(1-Methyl-1-phenylethyl)pyridine ((py)CMe₂Ph). 2-Benzylpyridine (0.1 mol) in diethyl ether (50 mL) was added slowly to a solution of phenyllithium (0.1 mol) in diethyl ether (200 mL) cooled in ice water. After this solution was stirred for 2 h, iodomethane (0.1 mol) in diethyl ether (20 mL) was added slowly to obtain a pale yellow solution. The solution was stirred for 12 h, water added cautiously, and the salt extracted with dilute HCl. The aqueous solution was neutralized with K₂CO₃ and extracted with diethyl ether. Diethyl ether was removed and the colorless oil treated again with 0.1 mol of phenyllithium and iodomethane. The product was distilled to give a colorless oil [bp 90 °C (0.1 mm), 85%]. Anal. Calcd for C₁₄H₁₅N: C, 85.2; H, 7.7; N, 7.1. Found: C, 85.2; H, 7.7; N, 7.1.

Tris(2-pyridyl)methane ((py)₂CH₂). (py)₂CH₂ was treated with phenyllithium in diethyl ether cooled in ice water, freshly distilled 2-bromopyridine added very slowly, benzene or toluene added, diethyl ether removed, and the solution refluxed for 12 h. On cooling this solution water was added, the benzene layer separated, and benzene removed by rotary evaporation. The residue was extracted with boiling petroleum (60-70 °C). The extract was treated with activated charcoal, and on filtration and cooling colorless crystals formed [15%, mp 98 °C (lit.²¹ mp 100-101 °C)].

***N*-Methyl-2-(2-pyridyl)imidazole (py-*N*-MeIm).** Dimethyl sulfate (1.9 mL) and sodium hydroxide (0.8 g) in water (2 mL) were added dropwise and simultaneously to a stirred ice-cold solution of 2-(2-pyridyl)imidazole (2.9 g) in methanol (10 mL). The solution was boiled for 30 min and methanol removed. Water (50 mL) was added and the product extracted with chloroform. The chloroform solution was dried and filtered, and chloroform was removed. The residue was dissolved in boiling petroleum (60-80 °C), treated with activated charcoal, and filtered, and petroleum was removed. Concentrated HCl (10 M, 6 mL) was added, the solution taken to dryness, and the hydrochloride salt recrystallized from ethanol. The required product was obtained as crystals on neutralization and extraction with diethyl ether [2 g, 63%, mp 34-35 °C (lit.¹⁷ mp 167 °C)]. Anal. Calcd for C₉H₉N₃: C, 67.9; H, 5.7; N, 26.4. Found: C, 66.6; H, 5.6; N, 25.7.

***N*-Methyl-2-(6-methyl-2-pyridyl)imidazole (6-Mepy-*N*-MeIm).** A similar procedure gave a colorless oil on evaporation of diethyl ether. Anal. Calcd for C₁₀H₁₁N₃: C, 69.3; H, 6.4; N, 24.3. Found: C, 69.4; H, 6.7; N, 23.6.

Preparation of Complexes. Methylmercuric nitrate was prepared as described previously.²³ Complexes were obtained in moderate yield

(37-82%) on addition of acetone solutions of methylmercuric nitrate to acetone solutions of the ligands. Complexes were generally crystalline and white and, except for complexes of *N*-benzylimidazole and 2-phenyl-*N*-methylimidazole which were recrystallized from methanol, did not require recrystallization. Complexes were prepared at ambient temperature, their solutions were not heated during recrystallization, and they were dried over P₂O₅. Attempted preparation of a complex with phenyldimethyl-2-picoline gave oils which could not be converted to a solid, and thus this complex has only been studied as an equimolar ratio of MeHgNO₃ and (py)CMe₂Ph in an NMR tube. The complexes were isolated, and their characterization data are summarized in Table I. ¹H NMR spectra of ligands and complexes have appropriate intensities, and full details of the spectra are recorded in Table VI (supplementary material). Microanalyses were by the Australian Microanalytical Service, Melbourne.

Physical Measurements. Infrared spectra (4000-400 cm⁻¹) of complexes in Nujol mulls between KBr plates were recorded with a Perkin-Elmer 577 spectrophotometer. ¹H NMR spectra at 100 MHz were measured on a JEOL JNM-4H-100 spectrometer. Chemical shifts in CD₃OD were measured relative to 1,4-dioxane as internal standard; shifts upfield of 1,4-dioxane are taken as negative.

Apparent protonation constants log *K*_H (p*K*_a of LH⁺) for all ligands were measured in 50% dioxane-water following an experimental procedure given earlier⁹ and are considered to be accurate to ± 0.05 log *K*_H units. For ligands containing one donor atom log *K*_H was calculated by the method of Albert and Serjeant²⁵ as before for monoacidic pyridines and 2,2'-bipyridyls.⁹ Both terpy²⁶ and (py)₂CH₂²⁰ are known to accept two protons, and as reported values for successive protonation constants of terpy (in water)²⁶ and (py)₂CH₂ (methanol)²⁰ differ by less than 2.7 log *K*_H units, the ionization processes must overlap,²⁵ and thus they cannot be calculated independently by the method of Albert and Serjeant.²⁵ For all potentially polyacidic bases a modified version²⁷ of the iterative nonlinear least-squares analysis of Schwartz and Gelb²⁸ was used. Agreement between calculated constants for the two methods was checked by calculating constants for unidentate ligands by both methods, e.g., Me₃-*N*-MeIm has log *K*_H = 8.25²⁵ and 8.28.²⁷ For potentially polyacidic bases, except for py-*N*-MeIm and 6-Mepy-*N*-MeIm which have basic sites close together (VI) as in monoacidic 2,2'-bipyridyls, the degree of fit was

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much better for treatment of the ligands as acceptors of two protons, e.g.; the equivalence point volume is refined as a least-squares parameter in the calculation and agrees with the expected value on formation of $(\text{pyH})(\text{py})\text{CH}_2^+$ from $(\text{py})_2\text{CH}_2$, but a value 14% too high is obtained on treatment of titration data as resulting from titration of a monoacidic base. However, as the values of $\log K_H$ obtained for addition of the second proton are less than or close to $-\log[\text{base}]$ ($\sim 2 \text{ mol dm}^{-3}$), the values calculated are not reliable,²⁵ so that the first protonation constants only are reported here (legend to Figure 2).

Crystallography. Unit cell parameters were determined with use of a Philips PW 1100 automatic four-circle diffractometer equipped with a graphite monochromator by a method described previously.²⁹ Intensity data were collected with use of colorless crystals that had been checked for cracking or twinning with a polarizing microscope. Crystals were mounted on a silica capillary with "Resiweld" epoxy cement.

For $[\text{MeHg}((\text{py})_2\text{CH}_2)]\text{NO}_3$ three standard reflections monitored at 1.5-h intervals showed no systematic variation in intensity, but for $[\text{MeHg}(\text{Et}_3\text{terpy})]\text{NO}_3$ three standard reflections (e.g., 400, 060, 004) monitored at 2-h intervals showed a small systematic decrease in intensity.

Data were collected by the ω -scan technique with a symmetric scan width of $\pm 1.00^\circ$ ($(\text{py})_2\text{CH}_2$ complex) and $\pm 0.65^\circ$ (Et_3terpy) in ω from the calculated Bragg angle, with an allowance for dispersion, at a scan rate of $0.05^\circ \text{ s}^{-1}$. The Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) was monochromatized with a flat graphite crystal, and no reflection was sufficiently intense to warrant the insertion of an attenuation filter. The data were processed with a program written specifically for the PW 1100 diffractometer.³⁰ The background corrected intensities were assigned standard deviations according to $\sigma(I) = [\text{CT} + (t_c/t_b)^2(B_1 + B_2) + (qI)^2]^{1/2}$, where CT is the total integrated peak count obtained in scan time t_c , B_1 and B_2 are background counts each obtained in time $1/2t_b$, and $I = \text{CT} - (t_c/t_b)(B_1 + B_2)$; q was 0.04 and is an allowance for "machine errors". Values of I and $\sigma(I)$ were then corrected for Lorentz and polarization effects.

$[\text{MeHg}((\text{py})_2\text{CH}_2)]\text{NO}_3$ (from Methanol): $\text{C}_{12}\text{H}_{13}\text{HgN}_3\text{O}_3$, $M_r = 447.84$, monoclinic, $a = 16.875(2) \text{ \AA}$, $b = 8.540(1) \text{ \AA}$, $c = 9.353(1) \text{ \AA}$, $\beta = 96.544(8)^\circ$, $V = 1339.10 \text{ \AA}^3$, $Z = 4$, $D_c = 2.221 \text{ g cm}^{-3}$, $D_m = 2.22(2) \text{ g cm}^{-3}$, $F(000) = 840$, space group $P2_1/n$ (No. 14 C_{2h}^2) from systematic absences $h0l$, $h + l$ odd, and $0k0$, k odd. This alternative setting of space group $P2_1/c$ was used for both structure determinations for convenience as β is closer to 90° . An absorption correction was applied on the basis of the indexed crystal faces (100), (100), (010), (010), (001), (101), and (101) and direction cosines calculated for the PW 1100 data. Maximum and minimum values of transmission factors were 0.5198 and 0.3836, respectively. The total number of reflections measured to $2\theta(\text{Mo } K\alpha) = 60^\circ$ for a crystal of dimensions ca. $0.09 \times 0.09 \times 0.11 \text{ mm}$ (optimum size 0.17 mm) was 4259; of these 258 were rejected as being systematically absent or having zero F or I and 116 were multiple observations [the measure of agreement between these, R , was 0.089 where R is given by $[\sum(N\sum(w(F_{av} - F)^2)) / \sum((N-1)\sum(wF^2))]^{1/2}$ (the inner summations are over the N equivalent reflections averaged to give F_{av} , and the outer summations are over all unique reflections)]. This left 3885 unique reflections of which 1154 obeyed the condition $I \geq 3\sigma(I)$, and 12 reflections were considered as poorly calculating, very weak reflections, and were omitted during refinement. Thus, 1142 reflections were used in the final refinement.

$[\text{MeHg}(\text{Et}_3\text{terpy})]\text{NO}_3$ (from Ethanol): $\text{C}_{22}\text{H}_{26}\text{HgN}_4\text{O}_3$, $M_r = 595.06$, monoclinic, $a = 9.115(2) \text{ \AA}$, $b = 15.725(3) \text{ \AA}$, $c = 15.566(3) \text{ \AA}$, $\beta = 94.465(14)^\circ$, $V = 2224.34 \text{ \AA}^3$, $Z = 4$, $D_c = 1.776 \text{ g cm}^{-3}$, $D_m = 1.77(2) \text{ g cm}^{-3}$, $F(000) = 1160$, space group $P2_1/n$ from systematic absences $h0l$, $h + l$ odd, and $0k0$, k odd. An absorption correction was applied on the basis of the indexed crystal faces (011), (011), (203), (203), (011), and (011), and direction cosines were calculated for the PW 1100 data. Maximum and minimum values of transmission factors were 0.5663 and 0.4029, respectively. The total number of reflections measured to $2\theta(\text{Mo } K\alpha) = 60^\circ$ for a crystal of dimensions $0.10 \times 0.15 \times 0.15 \text{ mm}$ (optimum size 0.30 mm) was 7062; of these 236 were rejected as being systematically absent or

Table II. Fractional Coordinates and Thermal Parameters for the Mercury Atom ($\times 10^4$) and Nonhydrogen Atoms ($\times 10^3$) in $[\text{MeHg}((\text{py})_2\text{CH}_2)]\text{NO}_3^a$

atom	x/a	y/b	z/c	U_{11}
Hg	2110 (1)	3400 (1)	4644 (1)	
C(1)	119 (1)	224 (3)	336 (2)	63 (7)
C(2)	330 (1)	399 (2)	738 (2)	39 (5)
C(3)	388 (1)	468 (2)	819 (2)	45 (6)
C(4)	448 (1)	565 (2)	751 (2)	52 (6)
C(5)	433 (1)	588 (2)	608 (2)	50 (6)
C(6)	367 (1)	529 (3)	532 (2)	50 (6)
C(7)	272 (1)	303 (2)	804 (2)	41 (6)
C(2')	198 (1)	393 (2)	828 (2)	36 (5)
C(3')	187 (1)	453 (2)	966 (2)	36 (5)
C(4')	117 (1)	534 (3)	976 (2)	58 (6)
C(5')	64 (1)	561 (3)	853 (2)	54 (6)
C(6')	83 (1)	501 (3)	727 (2)	51 (6)
N(1)	315 (1)	430 (2)	594 (2)	35 (4)
N(2)	149 (1)	704 (2)	329 (2)	63 (6)
N(1')	149 (1)	424 (2)	712 (2)	44 (5)
O(1)	142 (1)	820 (3)	253 (2)	98 (6)
O(2)	212 (1)	627 (2)	329 (2)	92 (6)
O(3)	99 (1)	662 (3)	396 (2)	108 (6)

^a Mercury refined anisotropically: $U_{11} = 454(5)$, $U_{22} = 436(5)$, $U_{33} = 403(4)$, $U_{12} = 9(8)$, $U_{13} = -75(3)$, $U_{23} = -61(7)$. Thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

having zero F or I and 342 were multiple observations ($R = 0.047$), leaving 6464 unique reflections of which 1297 obeyed the condition $I \geq 3\sigma(I)$, and 11 very weak reflections which were considered as poorly calculating ($F_o > 3F_c$) were omitted during refinement. Thus, 1286 reflections were used in the final refinement. The relatively small number of observed reflections arises as a consequence of the very small volumes of the data crystals.

For both complexes the Patterson synthesis enabled location of the mercury atom by standard methods; the mercury atom position was refined, and all nonhydrogen atoms were located in the subsequent difference Fourier syntheses. The function minimized in full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where w is the weight $[1/\sigma^2(F_o)]$ and F_o and F_c are the observed and calculated structure factors, respectively. Several cycles, with the mercury atom refined anisotropically and other nonhydrogen atoms refined isotropically, resulted in $R = 0.061$ ($(\text{py})_2\text{CH}_2$ complex) and 0.075 (Et_3terpy complex), where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. Absorption corrections were applied and several cycles of full-matrix, least-squares refinement led to $R = 0.60$ and 0.69 , and $R' = 0.053$ and 0.060 (for observed reflections), where $R' = \sum w^{1/2}(|F_o| - |F_c|) / \sum w^{1/2}|F_o|$. Insufficient data were available to enable refinement of these structures with anisotropic thermal parameters for all nonhydrogen atoms. Although difference Fourier syntheses revealed some hydrogen atom positions, all coordinates were calculated according to the geometry of the carbon atom to which they are bonded ($\text{C-H} = 1.08 \text{ \AA}$) and all hydrogen atoms were assigned isotropic thermal parameters.

Final refinements with hydrogen atoms riding on their respective carbon atoms involved 88 ($(\text{py})_2\text{CH}_2$ complex) and 141 (Et_3terpy) variables and gave $R = 0.054$ and 0.063 and $R' = 0.048$ and 0.055 , respectively. Final difference syntheses had no major characteristic greater than 1.89 e \AA^{-3} ($(\text{py})_2\text{CH}_2$) and 1.53 e \AA^{-3} (Et_3terpy), these occurring in the vicinity of the mercury atom; the largest shift to esd ratio in the final cycles was 0.113 for the C(1) z parameter ($(\text{py})_2\text{CH}_2$) and -0.749 for the C(8'') z parameter (Et_3terpy).

Final parameters for all nonhydrogen atoms are listed in Tables II and III, together with their estimated standard deviations, which were derived from the inverse least-squares matrix.

Refinements of the model for the Et_3terpy complex were carried out with use of the data set corrected for the small amount of decomposition (vide infra) that occurred and the uncorrected data set. The correction for decomposition made no significant improvement to the final structure, thus the refinement reported uses data uncorrected for decomposition.

In view of the relatively small number of observed data, having $I \geq 3\sigma(I)$, the final cycles of refinement were repeated with use of a data set for which the unobserved level was set at $I \geq \sigma(I)$ for

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Table III. Fractional Coordinates and Thermal Parameters for the Mercury Atom ($\times 10^4$) and for Other Nonhydrogen Atoms ($\times 10^3$) in $[\text{MeHg}(\text{Et}_3\text{terpy})]\text{NO}_3^a$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> ₁₁
Hg	3669 (1)	3353 (1)	207 (1)	
C(1)	389 (3)	207 (2)	-2 (2)	93 (10)
C(2)	477 (3)	478 (2)	166 (2)	67 (8)
C(3)	514 (3)	514 (2)	249 (2)	78 (8)
C(4)	619 (3)	465 (2)	298 (2)	81 (9)
C(5)	682 (3)	395 (2)	272 (2)	89 (10)
C(6)	632 (3)	362 (2)	191 (2)	67 (8)
C(7)	671 (4)	498 (2)	392 (2)	152 (15)
C(8)	617 (5)	570 (3)	407 (3)	211 (21)
C(2')	367 (3)	522 (2)	100 (2)	64 (8)
C(3')	333 (3)	605 (2)	113 (2)	74 (8)
C(4')	229 (3)	643 (2)	55 (2)	80 (9)
C(5')	171 (3)	601 (2)	-16 (2)	79 (9)
C(6')	213 (3)	513 (2)	-23 (2)	71 (8)
C(7')	216 (5)	743 (3)	57 (3)	158 (16)
C(8')	94 (6)	752 (3)	91 (3)	228 (23)
C(2'')	158 (3)	465 (2)	-107 (2)	59 (7)
C(3'')	39 (3)	491 (2)	-160 (2)	68 (8)
C(4'')	2 (3)	446 (2)	-233 (2)	73 (8)
C(5'')	84 (4)	379 (2)	-248 (2)	107 (11)
C(6'')	199 (3)	355 (2)	-196 (2)	103 (10)
C(7'')	-131 (4)	477 (2)	-293 (2)	110 (11)
C(8'')	-103 (5)	527 (3)	-365 (3)	186 (18)
N(1)	530 (2)	405 (1)	138 (1)	72 (7)
N(1')	310 (2)	475 (1)	32 (1)	56 (6)
N(1'')	236 (2)	398 (1)	-121 (1)	73 (7)
N(2)	98 (5)	269 (3)	179 (2)	150 (13)
O(1)	-22 (4)	264 (2)	201 (2)	169 (11)
O(2)	137 (3)	325 (2)	128 (1)	130 (8)
O(3)	172 (4)	208 (2)	184 (2)	194 (13)

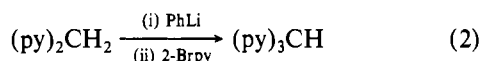
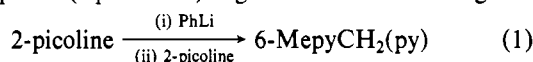
^a Mercury refined anisotropically: $U_{11} = 889$ (9), $U_{22} = 472$ (6), $U_{33} = 698$ (7), $U_{12} = 26$ (11), $U_{13} = 54$ (6), $U_{23} = -34$ (9).

comparison purposes. The agreement factors were $R = 0.133$ ($(\text{py})_2\text{CH}_2$, 2158 reflections) and 0.198 (Et_3terpy , 2810 reflections) and $R' = 0.088$ and 0.120 . The observation that virtually no changes occurred in the parameters, or their esd's, confirms the use of the cut-off value $I \geq 3\sigma(I)$ for structure determination.

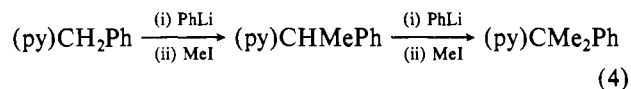
Atomic scattering factors for neutral atoms and corrections for anomalous dispersion were taken from Cromer et al.³¹ All calculations were performed on the Monash University B6700 computer. The major programs used were SHELX-76,³² ORFFE,³³ and MEANPL,³⁴ and figures were drawn with use of ORTEP.³⁵

Results and Discussion

A. Synthesis of Ligands and Complexes. Preparation of ligands of groups I, IV, V, and VI were as reported,^{15,17-19} with modifications for group VI. The ligand $(\text{py})_2\text{CH}_2$ was prepared from 2-picollythium and pyridine as reported,²⁰ and with use of similar procedures related ligands (6-methyl-2-pyridyl)(2-pyridyl)methane (6-MepyCH₂(py)) and $(\text{py})_3\text{CH}$ were prepared (eq 1 and 2) together with the new ligands



$(\text{py})_2\text{CR}_2$ ($R = \text{Me, Et}$) and 2-(1-methyl-1-phenylethyl)-pyridine $(\text{py})\text{CMe}_2\text{Ph}$ (eq 3 and 4).

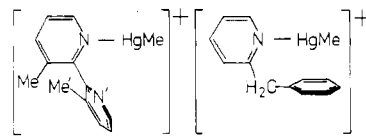


Methylmercury(II) derivatives were isolated by addition reactions in acetone (eq 5), and IR spectra indicate presence



of MeHg^{II} , nitrate, and ligand moieties with IR absorptions altered from those of the free ligand and MeHgNO_3 . Strong broad absorption in the region $1430\text{--}1300\text{ cm}^{-1}$ is characteristic of uncoordinated or weakly coordinated nitrate ions,³⁶ as found in crystal structure analyses of the related pyridine,¹¹ 3,3'-dmbpy,³⁷ and 2-benzylpyridine³⁸ complexes. A very weak absorption near 1750 cm^{-1} in the majority of spectra indicates that some KNO_3 from ion exchange with the KBr plates is also present. For most of the complexes $\nu(\text{Hg-C})$ can be assigned in the range $570\text{--}522\text{ cm}^{-1}$ (Table I).

B. Structures of Complexes in Solution. The ¹H NMR method relies on two approaches.^{9,14} (1) The chemical shift of the MeHg^{II} proton indicates whether (at least) one potential donor ring of the ligand is shielding that proton by ring current anisotropy. This approach is expected to be reliable if the uncoordinated ring must assume an orientation that shields the proton, e.g., for the 3,3'-dmbpy complex (VII) the MeHg^{II}



VII

VIII

proton resonance occurs 0.2–0.4 ppm upfield of other pyridine and 2,2'-bipyridyl complexes, and for ligands of groups I–VI is expected to be reliable for groups I and VI. Unless presence of shielding is indicated, e.g., for the 2-benzylpyridine complex (VIII), this method is not expected to be reliable for ligands like II and III where an uncoordinated ring could assume a conformation well removed from MeHg^{II} . Similar upfield shifts occur in other MeHg^{II} complexes,³⁹⁻⁴³ and the presence of anisotropic shielding is supported by crystal structures for $\text{MeHgN}^+\text{H}_2\text{CH}(\text{CO}_2^-)\text{CH}_2(p\text{-OHPh})$ ⁴⁴ and $[\text{MeHgL}]\text{NO}_3$ [$L = 3,3'\text{-dmbpy}$ (VII)³⁷ and 2-benzylpyridine (VIII)³⁸]. Orientation of the rings in this manner apparently results, at least partly, from presence of weak π interaction between mercury and the rings.^{37,38,41,44} (2) Comparison of $^2J(^1\text{H-}^{199}\text{Hg})$ with values for closely related unidentate ligands indicates whether the potential chelate is present as a unidentate. Thus, $^2J(^1\text{H-}^{199}\text{Hg})$ for the 3,3'-dmbpy complex lies on the $^2J(^1\text{H-}^{199}\text{Hg})$, $\log K_{\text{H}}$ line for pyridines, but bidentate 2,2'-bipyridyls have higher values of $^2J(^1\text{H-}^{199}\text{Hg})$ for similar $\log K_{\text{H}}$ values (Figure 1). This approach is expected to be applicable for II, III, and V and VI after determination of $^2J\text{-}$

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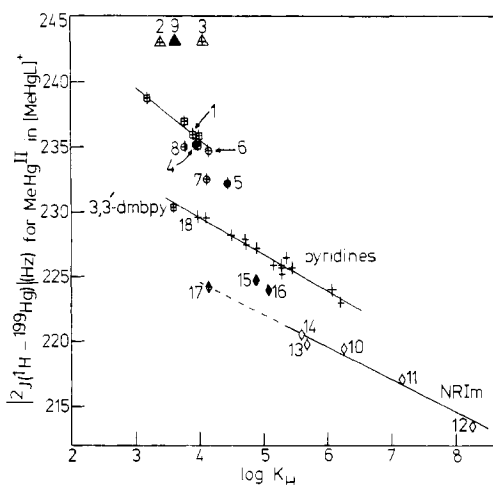
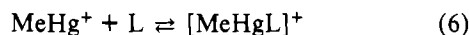


Figure 1. ${}^2J(^1\text{H}-^{199}\text{Hg})$ for $[\text{MeHgL}]\text{NO}_3$ (ca. 0.1 M in CD_3OD) vs. $\log K_{\text{H}}$ for the ligands (L). $\log K_{\text{H}}$ values are those obtained for a 50% dioxane-water mixture as solvent: (+) L = pyridines, except for (py)CMe₂Ph (O); (Δ) L = 2,2'-bipyridyls; (O) L = 2,2':6',2''-terpyridyls; (●) (py)₂CH₂ and 6-MepyCH₂(py); (□) (py)₂CR₂ (R = Me, Et); (▲) (py)₃CH; (◇) N-alkylimidazoles; (◊) N-pyIm; (♦) py-N-MeIm and 6-Mepy-N-MeIm. Values of ${}^2J(^1\text{H}-^{199}\text{Hg})$ for new complexes (1-17) are given in Table II, values of ${}^2J(^1\text{H}-^{199}\text{Hg})$ and $\log K_{\text{H}}$ for other complexes are given elsewhere.¹⁴ Ligands with $\log K_{\text{H}}$ values in parentheses are (1) 4,4'-Et₂(bpy) (3.90), (2) terpy (3.39), (3) Et₃terpy (4.03), (4) (py)₂CH₂ (3.94), (5) 6-MepyCH₂(py) (4.43), (6) (py)₂CMe₂ (3.88), (7) (py)₂CEt₂ (4.10), (8) (py)CMe₂Ph (3.76), (9) (py)₃CH (3.61), (10) N-MeIm (6.25), (11) 2-Me-N-MeIm (7.15), (12) Me₃-N-MeIm (8.24), (13) 2-Ph-N-MeIm (5.67), (14) N-BzIm (5.58), (15) py-N-MeIm (4.88), (16) 6-Mepy-N-MeIm (5.06), and (17) N-py-Im (4.13). Abbreviations for ligands are given with Table I and structures I-VI. For pyridines (+), ${}^2J(^1\text{H}-^{199}\text{Hg}) = -2.83 \log K_{\text{H}} + 240.9$ Hz (correlation coefficient -0.98);¹⁴ for 2,2'-bipyridyls (Δ), except 3,3'-dmbpy, ${}^2J(^1\text{H}-^{199}\text{Hg}) = -4.05 \log K_{\text{H}} + 251.8$ Hz (correlation coefficient -0.96); for N-alkylimidazoles (◇), ${}^2J(^1\text{H}-^{199}\text{Hg}) = -2.50 \log K_{\text{H}} + 234.6$ Hz (correlation coefficient -0.98).

(¹H-¹⁹⁹Hg) vs. $\log K_{\text{H}}$ for IV, but requires caution for I where the site of monoprotonation ($\log K_{\text{H}}$) may differ from the site of MeHg^{II} binding as there are two pyridyl environments. As this approach depends on comparison with results for unidentate ligands the appropriate $\log K_{\text{H}}$ value is monoprotonation, and for polyacidic bases evaluation of $\log K_{\text{H}}$ requires care in mathematical treatment of titration data (see Experimental Section).

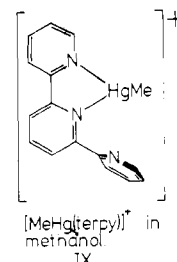
As expected, binding of the MeHg^{II} electrophile to all of the ligands results in downfield shifts of ligand proton resonances (Table VI, supplementary material), and as MeHg^{II} is a very labile cation,⁵ rapid equilibrium (eq 6) ensures av-



eraging of proton environments in potential chelates, e.g., H_nn' for terpy's (I). Appreciable values of stability constants for complexes of MeHg^{II} with pyridine ($\log K = 4.8^{45}$ and 4.72^{46}), 2,2'-bipyridyl ($\log K = 5.86^{47}$ and 5.93^{46}), terpy ($\log K = 6.35$),⁴⁶ and N-MeIm ($\log K = 6.96$)⁵ ensure that observed spectra result from $[\text{MeHgL}]^+$ with insignificant contributions from MeHg⁺ and L.

(1) **Complexes with terpy and Et₃terpy** have ${}^2J(^1\text{H}-^{199}\text{Hg}) = 243.0$ and 243.1 Hz, respectively, well removed from values for unidentate pyridines (Figure 1), and hence these ligands are not acting as unidentates via the *outer* pyridine ring—expected to be more basic than the central ring and thus the site of protonation in $\log K_{\text{H}}$ determinations. The coupling

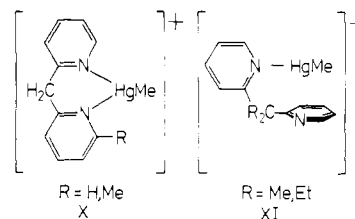
constants are also much larger than expected for unidentate binding via the central nitrogen as a simple Hammett calculation for terpy indicates the central nitrogen has $\log K_{\text{H}} \approx 2.27$, giving an expected ${}^2J(^1\text{H}-^{199}\text{Hg})$ for unidentate binding of 234.5 Hz,⁴⁸ well below the observed value (243 Hz). The MeHg^{II} ¹H resonances are 0.31–0.44 ppm upfield from bidentate 2,2'-bipyridyl complexes, indicating that (at least) one pyridyl ring is uncoordinated, and as they are not present as unidentates, both terpy and Et₃terpy are present as bidentates in methanol (IX) with an uncoordinated ring in an orientation



similar to that in the 3,3'-dmbpy complex (VII). Although present as bidentates the coupling constants are higher than observed for bidentate 2,2'-bipyridyl complexes (Figure 1), and this may reflect presence of a different coordination *geometry* and binding by nitrogen donors (in terpys) of differing basicity with one of these (central) having a basicity lower than for any of the 2,2'-bipyridyls studied. Kinetic studies also suggest that terpy does not bind as a unidentate to MeHg^{II}.⁴⁶

The ligand 4,4'-Et₂(bpy), obtained as a byproduct in synthesis of Et₃terpy, acts as a bidentate as the complex has ${}^2J(^1\text{H}-^{199}\text{Hg})$ similar to other 2,2'-bipyridyl complexes (Figure 1, no. 1) and the MeHg^{II} ¹H resonance is not shifted upfield from values for pyridine complexes.

(2) **Complexes of (py)₂CH₂, 6-MepyCH₂(py), and (py)₂CR₂** (R = Me, Et) all have ${}^2J(^1\text{H}-^{199}\text{Hg})$ well above the ${}^2J(^1\text{H}-^{199}\text{Hg})$, $\log K_{\text{H}}$ line for pyridines (Figure 1, nos. 4-7) suggesting that these ligands are present as bidentates, and consistent with bidentate behavior for (py)₂CH₂ and 6-MepyCH₂(py) (X) the



MeHg^{II} resonance is not shifted upfield from values for unidentate pyridines. However, complexes of (py)₂CR₂ (R = Me, Et) have the ¹H resonance 0.17–0.46 ppm upfield from pyridine complexes, and thus these ligands are present as unidentates (XI).

Presence of (py)₂CR₂ as unidentates may result from steric constraint of the alkyl substituents, and the steric effect of the CR₂(py) group in the α position of the coordinated ring may affect the C-Hg-N bonding geometry and thus ${}^2J(^1\text{H}-^{199}\text{Hg})$. For a test of this proposal the new pyridine (py)CMe₂Ph was synthesized as it has an α substituent of identical steric bulk to CMe₂(py) in (py)₂CMe₂; it formed a complex with ${}^2J(^1\text{H}-^{199}\text{Hg}) = 235.0$, similar to that of (py)₂CMe₂ complex (234.7 Hz), and with the MeHg^{II} ¹H resonance 0.32–0.63 ppm upfield from other pyridine complexes. A similar steric effect is absent

(45) R. B. Simpson, *J. Am. Chem. Soc.*, **83**, 4711 (1961).

(46) G. Geier, I. Erni, and R. Steiner, *Helv. Chim. Acta*, **60**, 9 (1977).

(47) G. Anderegg, *Helv. Chim. Acta*, **57**, 1340 (1974).

(48) A Hammett calculation [J. Clark and D. D. Perrin, *Q. Rev.*, **18**, 295 (1964), and references therein] gives $\log K_{\text{H}}(\text{central N}) = 2 \log K_{\text{H}}(2,2'\text{-bipyridyl}) - \log K_{\text{H}}(\text{pyridine}) = (2 \times 3.18) - 4.09 = 2.27$, where $\log K_{\text{H}}$ values were measured in 50% dioxane-water.⁹ From ${}^2J(^1\text{H}-^{199}\text{Hg}) = 2.83 \log K_{\text{H}} + 240.9$, an expected value of ${}^2J(^1\text{H}-^{199}\text{Hg}) = 234.5$ Hz is obtained.

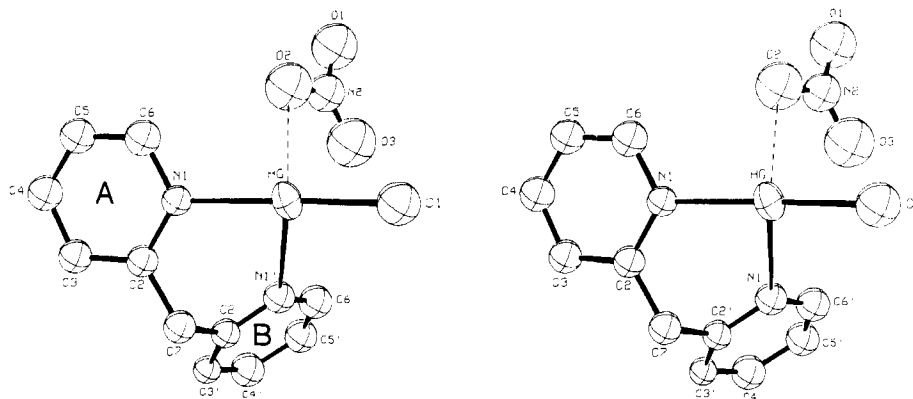
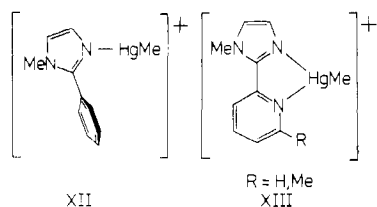


Figure 2. Structure of the cation $[\text{MeHg}(\text{py})_2\text{CH}_2]^+$ showing the relationship between Hg and the nearest nitrate ion.

for $(\text{py})_2\text{CH}_2$ and 6-Mepy $\text{CH}_2(\text{py})$ where the “ α -substituent” $\text{CH}_2(\text{py})$ has steric bulk identical with that of CH_2Ph in the 2-benzylpyridine complex (VIII), which has $\text{C}-\text{Hg}-\text{N} = 180$ (1°),³⁸ $^2J(^1\text{H}-^{199}\text{Hg})$ appropriate for pyridine complexes (Figure 1, no. 18), and the MeHg^{II} proton resonance 0.17–0.38 ppm upfield from other pyridine complexes.⁹

(3) **The $(\text{py})_3\text{CH}$ (III) complex** $[\text{MeHg}((\text{py})_3\text{CH})]\text{NO}_3$ has $^2J(^1\text{H}-^{199}\text{Hg})$ 243.1 Hz, higher than for pyridine, $(\text{py})_2\text{CH}_2$, and $(\text{py})_2\text{CR}_2$ complexes (Figure 1, no. 9), and the MeHg^{II} ^1H resonance is not shifted upfield from values for unidentate pyridines, consistent with presence of $(\text{py})_3\text{CH}$ as a tridentate (tripod) ligand. However, although $(\text{py})_3\text{CH}$ is clearly not present as a unidentate, molecular models indicate that for bidentate behavior the uncoordinated pyridyl ring is not constrained to be in an orientation resulting in shielding of the MeHg^{II} proton, although such an orientation is possible, so that the ^1H NMR method does not allow assignment of structure for this complex.

(4) **The N -alkylimidazoles (IV)** form linear complexes with $^2J(^1\text{H}-^{199}\text{Hg}) = -2.50 \log K_{\text{H}} + 234.6$ Hz and ca. 4 Hz lower than for pyridines of similar basicity (Figure 1). The cause of the decrease in coupling constants with increasing basicity of the donor groups has been discussed earlier for pyridine donors on the basis that the relative magnitude of $^2J(^1\text{H}-^{199}\text{Hg})$ is due mainly to the Fermi contact mechanism.⁹ The results for N -alkylimidazoles extend the general trend to higher values of $\log K_{\text{H}}$, and the slightly different relationships for these two types of donor presumably reflect the different character (s and p) of the nitrogen lone pair. The MeHg^{II} proton resonance occurs in the narrow range 2.61–2.67 ppm upfield from 1,4-dioxane, except for 2-Ph- N -MeIm which has an aromatic substituent able to shield the MeHg^{II} proton (XII, 2.80 ppm upfield) in the same manner as the uncoordinated pyridyl ring in the 3,3'-dmbpy complex (VII).⁴⁹



Consistent with bidentate behavior (XIII) ambidentate $\text{py}-N$ -MeIm and 6-Mepy- N -MeIm, which could potentially act as unidentates (via pyridyl or imidazolyl ring), form complexes with $\delta(\text{MeHg}^{\text{II}}) -2.61$, i.e., not shifted upfield from N -alkylimidazoles. Values of $\log K_{\text{H}}$ for these ligands presumably refer to the basicity of the imidazolyl nitrogen,⁵⁰ and

(49) The ligand N -benzylimidazole also has an uncoordinated aromatic ring, but it is well removed from the MeHg^{II} group on the “other side” of the imidazole ring and thus unable to shield the MeHg^{II} proton.

Table IV. Interatomic Distances (Å) and Angles (Deg) in $[\text{MeHg}(\text{py})_2\text{CH}_2]\text{NO}_3$

(a) Mercury Environment			
Hg-C(1)	2.10 (2)	Hg-N(1')	2.75 (2)
Hg-N(1)	2.16 (1)	Hg...O(2)	2.76 (2)
C(1)-Hg-N(1)	172 (1)	N(1)-Hg-N(1')	78 (1)
C(1)-Hg-N(1')	106 (1)	N(1)-Hg-O(2)	84 (1)
C(1)-Hg-O(2)	101 (1)	N(1')-Hg-O(2)	100 (1)
(b) Bis(2-pyridyl)methane Group			
ring A		ring B	
C(2)-N(1)	1.37 (2)	C(2')-N(1')	1.31 (2)
C(2)-C(3)	1.43 (3)	C(2')-C(3')	1.42 (3)
C(3)-C(4)	1.39 (3)	C(3')-C(4')	1.38 (3)
C(4)-C(5)	1.35 (3)	C(4')-C(5')	1.40 (3)
C(5)-C(6)	1.35 (3)	C(5')-C(6')	1.35 (3)
C(6)-N(1)	1.39 (3)	C(6')-N(1')	1.32 (3)
C(2)-C(7)	1.46 (3)	C(2')-C(7')	1.51 (3)
C(2)-N(1)-Hg	122 (1)	C(2')-N(1')-Hg	112 (1)
C(6)-N(1)-Hg	119 (1)	C(6')-N(1')-Hg	129 (1)
C(2)-N(1)-C(6)	119 (2)	C(2')-N(1')-C(6')	118 (2)
N(1)-C(2)-C(3)	119 (2)	N(1')-C(2')-C(3')	123 (2)
N(1)-C(2)-C(7)	118 (2)	N(1')-C(2')-C(7')	116 (2)
C(3)-C(2)-C(7)	123 (2)	C(3')-C(2')-C(7')	121 (2)
C(2)-C(3)-C(4)	120 (2)	C(2')-C(3')-C(4')	116 (2)
C(3)-C(4)-C(5)	119 (2)	C(3')-C(4')-C(5')	120 (2)
C(4)-C(5)-C(6)	121 (2)	C(4')-C(5')-C(6')	118 (2)
N(1)-C(6)-C(5)	122 (2)	N(1')-C(6')-C(5')	125 (2)
C(2)-C(7)-C(2')	113 (2)		
(c) Nitrate Ion			
N(2)-O(1)	1.22 (3)	N(2)-O(3)	1.18 (3)
N(2)-O(2)	1.24 (3)		
O(1)-N(2)-O(2)	117 (2)	O(2)-N(2)-O(3)	121 (2)
O(1)-N(2)-O(3)	122 (2)		

consistent with structure XIII values of $^2J(^1\text{H}-^{199}\text{Hg})$ lie above the $^2J(^1\text{H}-^{199}\text{Hg})$, $\log K_{\text{H}}$ line for N -alkylimidazoles (Figure 1, nos. 15 and 16)—an identical trend to that found for pyridyl donor ligands on increase in coordination number.

Correlations for unidentate pyridines and N -alkylimidazoles can be used to determine how the ambidentate ligand N -pyIm (V) binds to MeHg^{II} , as the complex has $^2J(^1\text{H}-^{199}\text{Hg})$ appropriate only for binding via the imidazole nitrogen (Figure 1, no. 17).⁵¹

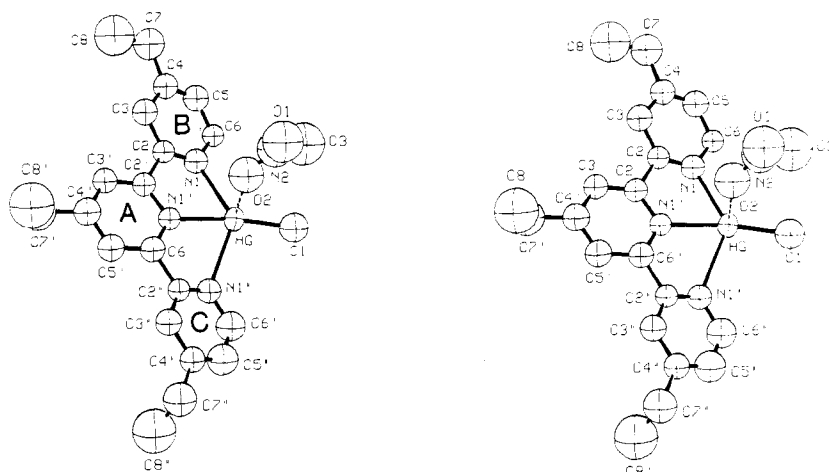
C. Crystallographic Studies of $[\text{MeHgL}]\text{NO}_3$ ($\text{L} = (\text{py})_2\text{CH}_2, \text{Et}_3\text{terpy}$). Aspects of the molecular geometry of these complexes are given in Tables V and VI, and different

(50) E.g., N -methylimidazole ($\log K_{\text{H}} = 6.25$) is more basic than pyridine ($\log K_{\text{H}} = 4.09$), and as imidazole and pyridine rings are electron-withdrawing groups, the pyridine nitrogen of $\text{py}-N$ -MeIm is expected to have $\log K_{\text{H}} < 4.09$ rather than the observed value of 4.88.

(51) For MeHg^{II} to be bonded to the pyridine ring with this coupling constant $\log K_{\text{H}}$ for the pyridine nitrogen would need to be ca. 5.9, well above the observed value for N -pyIm (4.88).

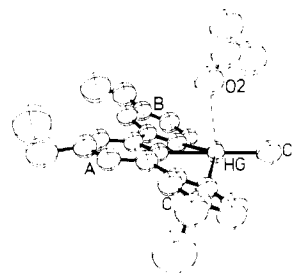
Table V. Interatomic Distances (Å) and Angles (Deg) in [MeHg(Et₃terpy)]NO₃

(a) Mercury Environment					
Hg-C(1)	2.06 (3)	Hg-N(1')	2.26 (2)	Hg...O(2)	2.78 (2)
Hg-N(1)	2.51 (2)	Hg-N(1'')	2.61 (2)		
C(1)-Hg-N(1)	119 (1)	N(1)-Hg-N(1')	69 (1)	N(1')-Hg-N(1'')	67 (1)
C(1)-Hg-N(1')	171 (1)	N(1)-Hg-N(1'')	131 (1)	N(1')-Hg-O(2)	80 (1)
C(1)-Hg-N(1'')	106 (1)	N(1)-Hg-O(2)	91 (1)	N(1'')-Hg-O(2)	102 (1)
C(1)-Hg-O(2)	98 (1)				
(b) Et ₃ terpy Group					
ring B		ring A		ring C	
C(2)-N(1)	1.33 (3)	C(6)-N(1)	1.37 (3)	C(2'')-N(1'')	1.30 (3)
C(2)-C(3)	1.43 (4)	C(4)-C(7)	1.59 (5)	C(2'')-C(3'')	1.37 (3)
C(3)-C(4)	1.41 (4)	C(7)-C(8)	1.27 (6)	C(3'')-C(4'')	1.36 (4)
C(4)-C(5)	1.32 (4)	C(2)-C(2')	1.53 (3)	C(4'')-C(5'')	1.32 (4)
C(5)-C(6)	1.41 (4)	C(3)-C(3')	1.37 (3)	C(5'')-C(6'')	1.33 (4)
		C(4)-C(4')	1.35 (4)	C(6'')-N(1'')	1.37 (4)
		C(5)-C(5')	1.39 (4)	C(7'')-C(8'')	1.55 (4)
		C(6)-C(6')	1.36 (4)	C(4'')-C(7'')	1.55 (4)
		C(7)-C(7')	1.44 (4)	C(5'')-C(6'')	1.33 (4)
C(2)-N(1)-Hg	113 (2)	C(2')-N(1')-Hg	121 (1)	C(2'')-N(1'')-Hg	113 (2)
C(6)-N(1)-Hg	124 (2)	C(6')-N(1')-Hg	122 (2)	C(6'')-N(1'')-Hg	127 (2)
C(2)-N(1)-C(6)	119 (2)	C(2)-N(1')-C(6')	116 (2)	C(2'')-N(1'')-C(6'')	116 (2)
N(1)-C(2)-C(3)	124 (2)	N(1')-C(2')-C(3')	124 (2)	N(1'')-C(2'')-C(3'')	124 (2)
N(1)-C(2)-C(2')	114 (2)	N(1')-C(2')-C(2)'	117 (2)	N(1'')-C(2'')-C(2)''	113 (2)
C(3)-C(2)-C(2')	121 (2)	C(3')-C(2')-C(2)'	119 (2)	C(3'')-C(2'')-C(2)''	123 (2)
C(2)-C(3)-C(4)	112 (2)	C(2')-C(3')-C(4)'	118 (2)	C(2'')-C(3'')-C(4)''	119 (2)
C(3)-C(4)-C(5)	125 (3)	C(3')-C(4')-C(5)'	121 (2)	C(3'')-C(4'')-C(5)''	117 (3)
C(3)-C(4)-C(7)	118 (3)	C(3')-C(4')-C(7)'	118 (3)	C(3'')-C(4'')-C(7)''	118 (2)
C(5)-C(4)-C(7)	117 (3)	C(5')-C(4')-C(7)'	118 (3)	C(5'')-C(4'')-C(7)''	125 (3)
C(4)-C(5)-C(6)	118 (3)	C(4')-C(5')-C(6)'	116 (2)	C(4'')-C(5'')-C(6)''	123 (3)
N(1)-C(6)-C(5)	121 (2)	N(1')-C(6')-C(5)'	123 (2)	N(1'')-C(6'')-C(5)''	121 (3)
C(4)-C(7)-C(8)	112 (3)	N(1')-C(6')-C(2'')	119 (2)	C(4'')-C(5'')-C(6'')	118 (3)
		C(5')-C(6')-C(2'')	117 (2)		
		C(4')-C(7')-C(8')	101 (4)		
(c) Nitrate Ion					
N(2)-O(1)	1.17 (6)	N(2)-O(2)	1.27 (5)	N(2)-O(3)	1.16 (5)
O(1)-N(2)-O(2)	123 (4)	O(1)-N(2)-O(3)	119 (4)	O(2)-N(2)-O(3)	114 (4)

Figure 3. Structure of the cation [MeHg(Et₃terpy)]⁺ showing the relationship between Hg and the nearest nitrate ion.

views of the structures are given in Figures 2-4. The structures are composed of [MeHgL]⁺ cations and regular (within 2σ) nitrate ions with one weak Hg...O(2) interaction [2.76 (2) (L = (py)₂CH₂) and 2.78 (2) Å (L = Et₃terpy)] in each structure. The MeHg^{II} group has Hg-C(1) = 2.10 (2) and 2.06 (3) Å, respectively, similar to that found in other MeHg^{II} complexes containing pyridyl donor groups [2.04 (3)¹¹ (L = py), 2.07 (5)¹⁰ (L = 2,2'-bipyridyl), 2.01 (1)³⁷ (L = 3,3'-dmbpy), 2.07 (3) Å³⁸ (L = 2-benzylpyridine)], and for both complexes pyridine rings are planar and regular.

In both the (py)₂CH₂ and Et₃terpy complexes MeHg^{II} is strongly bonded to one nitrogen at 2.16 (1) and 2.26 (2) Å, respectively, forming angles 172 (1) and 171 (1)° with that nitrogen (Figures 2 and 3; ring A in both complexes). Additional mercury-nitrogen distances of 2.75 (2) Å ((py)₂CH₂) and 2.51 (2) and 2.61 (2) Å (Et₃terpy) are well within the sum

Figure 4. Structure of [MeHg(Et₃terpy)]⁺ showing the angles between the pyridyl ring planes of Et₃terpy.

of van der Waals radii (3.23 Å),¹² so that (py)₂CH₂ is present as a bidentate and Et₃terpy as a tridentate. The CHgN₂ and CHgN₃ moieties are approximately planar with maximum

deviations from mean planes being 0.080 (1) Å (Hg) in the (py)₂CH₂ complex and -0.317 (19) Å [N(1')] in the Et₃terpy complex. The coordination geometry for the (py)₂CH₂ complex may be regarded as distorted "T shape" and for the Et₃terpy complex as highly distorted square planar.

Presence of a dominant, almost linear, C-Hg-N moiety with additional weak mercury-nitrogen bond(s), suggested from CHgN₂ and CHgN₃ geometry, is confirmed by consideration of the orientation of mercury with respect to the pyridine rings. Thus, for the strongly bound rings mercury is only -0.076 (1) and -0.121 (1) Å from plane A of (py)₂CH₂ and Et₃terpy, respectively, with Hg-N-C(2,6) angles 119 (1)-122 (1)°, but 0.469 (1) Å from the plane of ring B [angles 112 (1) and 129 (1)°] in the (py)₂CH₂ complex and -0.886 (1) and -1.032 (1) Å from the planes of ring B [113 (2), 124 (2)°] and ring C [113 (2), 127 (2)°], respectively, in the Et₃terpy complex (Figure 4). For the Et₃terpy complex angles between the planes of rings A and B (15.4°) and A and C (18.6°) are larger than in other terpy complexes, e.g., Co(terpy)Cl₂ (2.4, 4.9°)⁵² and Zn(terpy)Cl₂ (4.4, 6.0°).⁵³

As found for the three-coordinate 2,2'-bipyridyl complex, which also has irregular geometry based on a dominant C-Hg-N moiety [2.24 (3) Å, 164 (1)°] with a weaker additional Hg-N bond [2.43 (3) Å],¹⁰ even the shorter Hg-N bonds are longer than those in two-coordinate MeHg^{II} complexes of unidentate pyridines as follows: py, 2.12 (2);¹¹ 3,3'-dmbpy, 2.10 (2);³⁷ 2-benzylpyridine, 2.11 (1) Å.³⁸ As in the 2,2'-bipyridyl complex, the coordination geometry is consistent with essentially sp hybridization for mercury forming the dominant C-Hg-N axis, together with weaker interaction of the other donor lone pair(s) with a vacant 6p orbital of mercury.

It is of interest that terpys act as bidentates, like 2,2'-bipyridyls, in methanol but Et₃terpy acts as a tridentate in the solid state with MeHg^{II} most strongly bound to the nitrogen atom of lowest basicity. For (py)₂CR₂ (R = Me, Et) unidentate behavior in methanol was attributed to an increased steric effect of substitution at the methylene bridge, and consistent with this the weaker Hg-N(1') bond in [MeHg((py)₂CH₂)]NO₃ is longer than those in the 2,2'-bipyridyl and Et₃terpy complexes and is thus expected to be more susceptible to disruption by minor steric influences.

Summary

The following principal conclusions have been reached from the results of this investigation. (1) Examples of three-coordination for mercury observed in MeHg^{II} complexes of 2,2'-bipyridyls and rigid 1,10-phenanthrolines⁹ have been extended to involve a range of ligands that could also allow MeHg^{II} to assume the commonly observed linear two-coordination geometry for mercury. (2) Bis(2-pyridyl)methanes function as bidentate ligands toward MeHg^{II} in methanol and in the solid state. These ligands lack resonance stabilization between pyridine rings which may favor chelate behavior of 2,2'-bipyridyls. Dialkyl substitution of the methylene bridge

results in unidentate coordination and deviation from the ²J-(¹H-¹⁹⁹Hg), log K_H relationship for simple pyridine complexes. (3) 2,2':6',2''-Terpyridyls act as bidentates in methanol but as tridentates in the solid state to give a new coordination geometry for MeHg^{II}—highly distorted square planar based on a dominant C-Hg-N moiety. (4) *N*-Alkylimidazole complexes, [MeHgL]NO₃, form a linear ²J(¹H-¹⁹⁹Hg), log K_H relation different from that of pyridine complexes. This can be used to show that MeHg^{II} will accept ligands with a mixed pyridine/*N*-alkylimidazole donor set to form complexes with three-coordination for mercury. (5) This correlation can be used to determine the binding site to ambidentate ligands containing pyridyl and imidazolyl rings; in the ligand studied, *N*-(2-pyridyl)imidazole, MeHg^{II} binds to the imidazole ring. (6) Study of *N*-alkylimidazoles with log K_H extending to higher values than pyridines further confirms the general trend of decreasing ²J(¹H-¹⁹⁹Hg) with increasing basicity and provides more confidence in its application to other ligands, e.g., determination of binding sites in nucleosides and related molecules involving nitrogen donor sites of different character.^{23,54} (7) Use of MeHg^{II} and aromatic nitrogen donor ligands provides a method for studying (presumably) weak coordination interactions in the solution phase.

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Registry No. [MeHg(4,4'-Et₂(bpy))]NO₃, 77450-46-5; [MeHg(terpy)]NO₃, 77450-48-7; [MeHg(Et₃terpy)]NO₃, 74883-18-4; [MeHg((py)₂CH₂)]NO₃, 74893-24-6; [MeHg(6-MepyCH₂(py))]NO₃, 77450-50-1; [MeHg((py)₂CMe₂)]NO₃, 77450-52-3; [MeHg((py)₂CEt₂)]NO₃, 77450-54-5; [MeHg((py)₂CH)]NO₃, 77450-56-7; [MeHg(*N*-MeIm)]NO₃, 77450-57-8; [MeHg(2-Me-*N*-MeIm)]NO₃, 77450-59-0; [MeHg(Me₃-*N*-MeIm)]NO₃, 77450-29-4; [MeHg(2-Ph-*N*-MeIm)]NO₃, 77450-31-8; [MeHg(*N*-BzIm)]NO₃, 77450-33-0; [MeHg(py-*N*-MeIm)]NO₃, 77450-35-2; [MeHg(6-Mepy-*N*-MeIm)]NO₃, 77450-37-4; [MeHg(*N*-pyIm)]NO₃, 77450-39-6; [MeHg((py)CMe₂Ph)]NO₃, 77450-41-0; 6-MepyCH₂(py), 19087-66-2; (py)₂CEt₂, 77429-56-2; (py)₂CMe₂, 77429-57-3; (py)CMe₂Ph, 60025-44-7; (py)₃CH, 77429-58-4; py-*N*-MeIm, 77429-59-5; 6-Mepy-*N*-MeIm, 77429-60-8; 2-picoline, 109-06-8; (py)₂CEtH, 77429-61-9; 2-benzylpyridine, 101-82-6; (py)₂CH₂, 1132-37-2; 2-bromopyridine, 109-04-6; 2-(2-pyridyl)imidazole, 18653-75-3; Et₂bpy, 3052-28-6; terpy, 1148-79-4; Et₃terpy, 33354-77-7; *N*-MeIm, 616-47-7; 2-Me-*N*-MeIm, 1739-84-0; Me₃-*N*-MeIm, 1739-83-9; 2-Ph-*N*-MeIm, 3475-07-8; *N*-BzIm, 4238-71-5; *N*-pyIm, 25700-14-5.

Supplementary Material Available: ¹H NMR data and assignments for complexes and ligands (Table VI), a list of observed and calculated structure factors, calculated hydrogen atom positions, and thermal parameters (Tables VII and VIII), mean planes data (Table IX) for [MeHgL]NO₃ (L = (py)₂CH₂, Et₃terpy), and packing diagrams for [MeHg((py)₂CH₂)]NO₃ (Figure 5) and [MeHg(Et₃terpy)]NO₃ (Figure 6) (25 pages). Ordering information is given on any current masthead page.

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