to −20 °C produced an orange crystalline solid. Removal of the CH$_2$Cl$_2$ followed by drying afforded [Me$_2$NP(Cl)Fe(CO)$_4$]$^+$[AlCl$_4$]$^-$ in virtually quantitative yield (1.29 g, 2.89 mmol). Anal. Calcd for C$_6$H$_6$AlCl$_5$FeNO$_4$P: C, 16.11; H, 1.36; N, 3.13. Found: C, 15.77; H, 1.73; N, 3.00.

The following compounds were prepared in virtually quantitative yields by an analogous procedure.

[(Et$_2$N)$_2$PFe(CO)$_4$]$^+$[AlCl$_4$]$^-$ (2): orange solid. Anal. Calcd for C$_{12}$H$_{20}$AlCl$_4$FeN$_2$O$_4$P: C, 28.41; H, 4.19; N, 5.45. Found: C, 28.15; H, 3.95; H, 5.47.

[(*i*-Pr$_2$N)$_2$PFe(CO)$_4$]$^+$[AlCl$_4$]$^-$ (3): orange solid. Anal. Calcd for C$_{16}$H$_{28}$AlCl$_4$FeN$_2$O$_4$P: C, 33.83; H, 4.98; N, 4.93. Found: C, 33.27; H, 4.80; N, 5.10.

The compounds [((Me$_3$Si)$_2$N)$_2$PFe(CO)$_4$]$^+$[AlCl$_4$]$^-$ (4) and [(*t*-Bu)(Me$_2$N)PFe(CO)$_4$]$^+$[AlCl$_4$]$^-$ (5) were not stable above −20 °C; hence it was necessary to identify them by means of low-temperature NMR spectroscopy (see Table II and text).

Contribution from the Chemistry Departments, University of Tasmania, Hobart, Tasmania, Australia 7001, and Monash University, Clayton, Victoria, Australia 3168

Coordination Chemistry of Methylmercury(II). Complexes of Aromatic Nitrogen Donor Tripod Ligands Involving New Coordination Geometries for MeHg^{II}

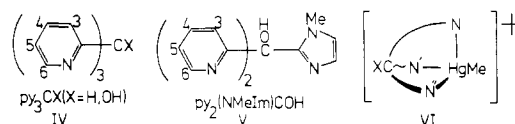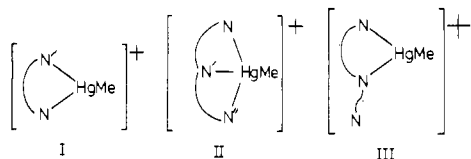ALLAN J. CANTY,*[1] NARONGSAK CHAICHIT,[2] BRYAN M. GATEHOUSE,*[2] and EDWIN E. GEORGE[1]

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Complexes [MeHgL]NO$_3$ {L = diphenyl(2-pyridyl)methane (pyCHPh$_2$), bis(2-pyridyl)phenylmethane [(py)$_2$CHPh], and the tripod ligands tris(2-pyridyl)carbinol [(py)$_3$COH] and bis(2-pyridyl)(*N*-methyl-2-imidazolyl)carbinol [(py)$_2$(*N*-MeIm)COH]} are obtained from addition reactions in acetone. The ligand (py)$_2$CHPh is formed on reaction of (2-benzylpyridyl)lithium with 2-bromopyridine. ^{1}H NMR spectra indicate that (py)$_2$CHPh and (py)$_2$(*N*-MeIm)COH are present as bidentates in methanol solutions of their complexes, with the latter coordinated via the imidazolyl ring and one pyridyl ring. Spectra are consistent with the presence of weak π interactions between mercury and phenyl rings in the (py)CHPh$_2$ and (py)$_2$CHPh complexes and the uncoordinated pyridyl ring in the (py)$_2$(*N*-MeIm)COH complex. In complexes [MeHgL]NO$_3$ (L = (py)$_3$COH, (py)$_3$CH) the ligands are present as tridentates in methanol. Crystalline [MeHgL]NO$_3$ [L = (py)$_3$COH, (py)$_2$(*N*-MeIm)COH] have the tripod ligands coordinating as tridentates, with irregular coordination geometries based on a dominant C–Hg–N' moiety [Hg–N' = 2.28 (1) Å, C–Hg–N' = 150 (1)° ((py)$_3$COH) and 2.13 (1) Å, 170 (0)° ((py)$_2$(*N*-MeIm)COH)] with weaker Hg–N,N'' bonds [2.45 (1), 2.53 (1) ((py)$_3$COH) and 2.66 (1), 2.71 (1) Å ((py)$_2$(*N*-MeIm)COH)]. For [MeHg((py)$_2$(*N*-MeIm)COH)] the coordination geometry resembles a trigonal bipyramid lacking one equatorial donor and with axial direction C–Hg–N' [crystal data: [MeHg((py)$_3$COH)]NO$_3$ space group *P*$\bar{1}$, Z = 2, a = 10.216 (4) Å, b = 12.628 (5) Å, c = 9.614 (3) Å, α = 103.71 (2)°, β = 129.67 (2)°, γ = 91.86 (3)°, R = 0.044 for 2107 reflections having $I \geq 3\sigma(I)$; [MeHg((py)$_2$(*N*-MeIm)COH)]NO$_3$ space group *P*$\bar{1}$, Z = 2, a = 11.739 (6) Å, b = 9.689 (2) Å, c = 8.182 (2) Å, α = 94.70 (4)°, β = 95.58 (2)°, γ = 97.00 (2)°, R = 0.042 for 2652 reflections having $I \geq 3\sigma(I)$].

Methylmercury(II) is regarded as an essentially unifunctional cation to give coordination number 2 for mercury,[3] although three-coordination is now well established in a series of complexes [MeHgL]NO$_3$ for both the solid state and solution where L are potentially uni- or bidentate ligands, e.g., 2,2'-bipyridyls,[4,5] bis(2-pyridyl)methanes,[6,7] and bis(*N*-pyrazolyl)methane (I).[8] In addition, 2,2':6',2''-terpyridyls act as tridentates in the solid state (II) but as bidentates in methanol (III).[6,7] The coordination geometry for mercury in these complexes involves a dominant C–Hg–N group close to linearity [C–Hg–N = 164 (1)–179 (1)°, Hg–N = 2.16 (1)–2.26 (2) Å] with weaker bonding to additional nitrogen atoms [2.43 (3)–2.96 (2) Å], consistent with essentially sp hybridization for mercury with weaker bonding via interaction of nitrogen lone pairs with one empty 6p orbital of mercury.

With this simplified bonding model as a guide "tripod" ligands such as IV and V may also be expected to encourage

coordination number 4 with a novel coordination geometry involving bonding of N and N'' to *both* empty 6p orbitals of mercury (VI). Also, ligands of this type satisfy two primary requirements followed in our earlier studies: they are flexible

(1) University of Tasmania.
(2) Monash University.
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and thus potentially able to act as unidentates, and application of a ^{1}H NMR method[4,7,9] appears feasible for determination of coordination behavior in solution. Initial studies with (py)$_3$CH led to isolation of a complex for which ^{1}H NMR results were consistent with tridentate behavior but did not allow definite assignment of structure, and crystals suitable for structural studies could not be obtained.[7]

We report here the isolation of complexes of tripod ligands, one of which ((py)$_3$COH) behaves as a tridentate both in the solid state and in methanol. Another tripod, (py)$_2$(N-MeIm)COH, acts as a tridentate in the solid state but is bidentate in methanol, illustrating the flexibility of these ligands.

Experimental Section

Reagents. Methylmercuric nitrate,[10] other reagents,[7] and solvents[7] were prepared and purified as described previously. Diphenyl(2-pyridyl)methane ((py)CHPh$_2$) was used as received (Cambrian Chemicals); (py)$_3$COH [(recrystallized from ethanol) mp 124–125 °C (lit.[11] mp 127–128 °C)] and (py)$_2$(N-MeIm)COH [(from benzene) mp 146–148 °C (lit.[12] mp 153–155 °C)] were prepared as described.[11,12]

Bis(2-pyridyl)phenylmethane ((py)$_2$CHPh). 2-Benzylpyridine (0.15 mol) in diethyl ester (25 mL) was added slowly with stirring to a solution of phenyllithium (0.15 mol) in diethyl ether (250 mL) under a nitrogen atmosphere and cooled in ice water. After this solution was stirred for 30 min, 2-bromopyridine (0.15 mol) in diethyl ether (50 mL) was added slowly at ambient temperature. Benzene (200 mL) was added, diethyl ether was removed by distillation, and the remaining solution was refluxed for 12 h. Water (200 mL) was added cautiously to the solution cooled in ice water, and after vigorous shaking the benzene layer was separated. Benzene was removed by rotary evaporation, and the residue was treated with boiling petroleum ether (300 mL, 60–80 °C) followed by activated carbon and K$_2$CO$_3$. When the mixture was filtered and the filtrate was cooled, a yellow oil separated and was discarded. The pale yellow solution resulting was cooled at 0 °C, and crystals were collected and recrystallized from petroleum ether [3.6 g (10% yield), mp 81.5–82.5 °C]. Anal. Calcd for C$_{17}$H$_{14}$N$_2$: C, 82.9; H, 5.7; N, 11.4. Found: C, 82.7; H, 5.8; N, 11.4. ^{1}H NMR: δ 4.76 d (H$_6$, $J_{5,6}$ ~ 6 Hz), 4.05 td (H$_4$, $J_{3,4}$ ~ $J_{4,5}$ ~ 7.7, $J_{4,6}$ = 1.7 Hz), 3.66–3.39 (H$_{3,5}$,Ph), 2.14 (CH) (Chemical shifts from 1,4-dioxane in CD$_3$OD). Mass spectrum: m/e 246 (parent ion, 70%).

Preparation of Complexes. Complexes were obtained as crystals in moderate yield (27–86%) at ambient tempeature on addition of acetone solutions of methylmercuric nitrate to acetone solutions of the ligands. The complexes were isolated, and their characterization data are summarized in Table I. Microanalyses were by the Australian Microanalytical Service, Melbourne.

Physical Measurements. ^{1}H NMR spectra at 100 MHz were measured on a JEOL JNM-4H-100 spectrometer. Chemical shifts in CD$_3$OD were measured relative to 1,4-dioxane (3.64 ppm from Me$_4$Si) as internal standards; shifts upfield of 1,4-dioxane are taken as negative. Apparent protonation constants log K_H (pK_a of LH$^+$) for all ligands were measured in 50% dioxane–water following an experimental procedure given earlier[7] and are considered to be accurate to ±0.05 log K_H unit.

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.[13] Intensity data were collected with use of colorless crystals that had been checked for twinning with a polarizing microscope. Crystals were mounted on a silica capillary with "Resiweld" epoxy cement.

For [MeHg((py)$_3$COH)]NO$_3$ three standard reflections (e.g., 200, 020, 002) monitored at 2-h intervals and for [MeHg((py)$_2$(N-MeIm)COH)]NO$_3$ three standard reflections (e.g., 700, 170, 105)

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Table I. Characterization Data for the Complexes[a]

complex	% calcd				% found				δ- (MeHg)[b]	^2J- (^{1}H– ^{199}Hg)[c]	δ(pyridyl protons)[b,d,e]					δ(other protons)[b]	J within ligand[e]
	C	H	Hg		C	H	Hg				H$_3$	H$_4$	H$_5$	H$_6$			
[MeHg((py)CHPh$_2$)]NO$_3$	43.6	3.5	38.4		43.8	3.5	38.0		−2.94	232.7	f	4.51 m	4.11 m	5.08 db		2.51 (CH)[f]	$J_{4,3} = J_{4,5} = 7.7, J_{5,6} \approx 4.8$
[MeHg((py)$_2$CHPh)]NO$_3$	41.3	3.3	38.3		41.3	3.3	38.1		−3.08	238.2	g	g	4.0 m	5.7 db		2.48 (CH)[g]	$J_{4,5} = 5.7$
[MeHg((py)$_3$COH)]NO$_3$	37.8	3.0	37.1		37.8	3.4	37.6		−2.69	240.7	h	h	3.93 m	4.94 db			$J_{5,6} \approx 4.9$
[MeHg((py)$_2$(N-MeIm)COH)]NO$_3$	35.6	3.5	37.0		35.6	3.5	37.0		−2.89	222.8	i	i	i	4.86 db		0.10 (NMe)[i]	$J_{5,6} \approx 5$

[a] Solutions in CD$_3$OD. [b] Chemical shifts from internal 1,4-dioxane; accuracy to ca. 0.005 ppm. Complexes of unidentate pyridines without aromatic substituents in the 2 position have δ(MeHg) = −2.47 to −2.68 ppm.[4,7,9] [c] Accuracy to ca. ±0.5 Hz. [d] Key: m, multiplet; d, doublet; b, broad. [e] First-order analysis.[4] [f] 3.4–4.25 mb (H$_{3,5}$, Ph). [g] 3.4–4.81 mb (H$_{3,4}$), 3.66–3.84 mb (Ph). [h] 4.3–4.6 mb (H$_{3,4}$). [i] 3.54–4.39 (H$_{3,4,5,4',5'}$).

Table II. Fractional Coordinates and Thermal Parameters^a ($\times 10^4$) for Mercury and ($\times 10^3$) for Other Nonhydrogen Atoms in [MeHg((py)$_3$COH)]NO$_3$

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	1340 (1)	3290 (1)	1898 (1)	389 (3)	970 (4)	573 (3)	140 (2)	349 (2)	385 (3)
C(1)	321 (2)	375 (1)	182 (2)	61 (8)	159 (15)	125 (12)	49 (9)	71 (9)	102 (11)
C(2)	-153 (1)	120 (1)	100 (1)	39 (6)	35 (7)	47 (6)	22 (5)	26 (5)	18 (6)
C(3)	-290 (1)	24 (1)	-4 (2)	39 (6)	38 (8)	67 (8)	-1 (6)	26 (6)	14 (7)
C(4)	-350 (2)	-41 (1)	-184 (2)	63 (9)	46 (9)	51 (9)	6 (7)	10 (7)	-6 (8)
C(5)	-272 (2)	-10 (1)	-246 (2)	101 (12)	68 (11)	56 (9)	36 (10)	46 (10)	10 (9)
C(6)	-135 (2)	85 (1)	-133 (2)	66 (8)	56 (9)	43 (7)	34 (7)	30 (7)	15 (7)
C(7)	-92 (1)	200 (1)	292 (1)	34 (5)	42 (7)	41 (6)	9 (5)	26 (5)	16 (6)
C(2')	-134 (1)	316 (1)	267 (1)	28 (5)	36 (7)	29 (5)	7 (5)	18 (4)	7 (5)
C(3')	-250 (1)	352 (1)	287 (1)	46 (6)	34 (7)	54 (7)	17 (5)	37 (6)	16 (6)
C(4')	-290 (1)	453 (1)	259 (2)	49 (7)	52 (8)	55 (7)	18 (6)	37 (6)	18 (6)
C(5')	-219 (2)	513 (1)	211 (2)	68 (8)	31 (7)	52 (7)	14 (6)	42 (6)	6 (6)
C(6')	-105 (1)	469 (1)	193 (1)	40 (6)	44 (8)	35 (6)	4 (5)	24 (5)	5 (6)
C(2'')	105 (1)	210 (1)	457 (1)	38 (5)	26 (6)	35 (5)	8 (5)	23 (5)	11 (5)
C(3'')	157 (1)	155 (1)	589 (2)	64 (8)	44 (8)	86 (9)	28 (6)	53 (7)	46 (7)
C(4'')	335 (2)	166 (1)	733 (2)	69 (9)	85 (10)	66 (8)	36 (8)	36 (7)	59 (8)
C(5'')	455 (2)	232 (1)	748 (2)	43 (7)	70 (9)	49 (7)	19 (6)	23 (6)	27 (7)
C(6'')	394 (1)	280 (1)	611 (1)	37 (6)	45 (7)	37 (6)	11 (5)	22 (5)	8 (6)
N(1)	-76 (1)	150 (1)	39 (1)	50 (5)	42 (6)	33 (5)	15 (4)	24 (4)	10 (5)
N(2)	-200 (1)	292 (1)	-328 (1)	39 (6)	62 (7)	45 (6)	3 (5)	26 (5)	16 (6)
N(1')	-62 (1)	374 (1)	223 (1)	36 (4)	30 (5)	40 (5)	9 (4)	26 (4)	14 (4)
N(1'')	221 (1)	271 (1)	468 (1)	32 (4)	36 (5)	40 (5)	9 (4)	24 (4)	15 (4)
O	-193 (1)	149 (1)	322 (1)	46 (5)	45 (5)	66 (6)	3 (4)	41 (5)	22 (5)
O(1)	-80 (1)	262 (1)	-323 (1)	68 (6)	97 (7)	61 (5)	33 (5)	48 (5)	32 (5)
O(2)	-169 (1)	348 (1)	-185 (1)	75 (6)	133 (9)	48 (5)	36 (6)	43 (5)	11 (6)
O(3)	-348 (1)	265 (1)	-484 (1)	53 (6)	158 (10)	69 (7)	-2 (6)	40 (6)	-3 (6)

^{a} Thermal parameters (Å^2) are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

monitored at 1.5-h intervals showed no systematic variation in intensity.

Data were collected by the ω-scan technique with a symmetric scan width of $\pm 0.65°$ in ω from the calculated Bragg angle, with an allowance for dispersion, at a scan rate of 0.05° s^{-1} for both complexes. The Mo Kα radiation ($\lambda = 0.7107$ Å) 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.[14] The background-corrected intensities were assigned standard deviations according to $\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (qI)^2]^{1/2}$ 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 $^1/_2 t_b$, and $I = CT - (t_c/t_b)(B_1 + B_2)$; 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.

[MeHg((py)$_3$COH)]NO$_3$: C$_{17}$H$_{16}$N$_4$O$_4$Hg, $M_r = 540.93$, triclinic, $a = 10.216$ (4) Å, $b = 12.628$ (5) Å, $c = 9.614$ (3) Å, $\alpha = 103.71$ (2)°, $\beta = 129.67$ (2)°, $\gamma = 91.86$ (3)°, $V = 899.05$ Å^3, $Z = 2$, μ(Mo Kα) = 82.59 cm^{-1}, $D_c = 1.998$ g cm^{-3}, $D_m = 2.01$ (2) g cm^{-3}, $F(000)$ = 516, space group $P\bar{1}$ (No. 2, C_i^1). An absorption correction was applied on the basis of the indexed crystal faces ($0\bar{1}0$), ($11\bar{1}$), ($0\bar{1}0$), ($\bar{1}\bar{1}1$), ($1\bar{1}1$), ($\bar{1}1\bar{1}$), and ($2\bar{6}\bar{1}$) and direction cosines calculated for the PW 1100 data. Maximum and minimum values of transmission factors were 0.6819 and 0.3171, respectively. The total number of reflections measured to 2θ(Mo Kα) = 60° for a crystal of dimensions ca. 0.05 $\times$ 0.13 $\times$ 0.23 mm (optimum size 0.24 mm) was 5234; of these no reflections were rejected as being systematically absent or having zero F or I and 288 were multiple observations (the measure of agreement between these, R, was 0.038 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 4946 unique reflections of which 2115 obeyed the condition $I \geq 3\sigma(I)$. Eight very weak reflections, considered as poorly calculating ($F_o > 3F_c$), were omitted during refinement. Thus, 2107 reflections were used in the final refinement.

[MeHg((py)$_2$(N-MeIm)COH)]NO$_3$: C$_{16}$H$_{17}$N$_5$O$_4$Hg, $M_r = 543.93$, triclinic, $a = 11.739$ (6) Å, $b = 9.689$ (2) Å, $c = 8.182$ (2) Å, $\alpha = 94.70$ (4)°, $\beta = 95.58$ (2)°, $\gamma = 97.00$ (2)°, $V = 915.15$ Å^3, $Z = 2$, μ(Mo Kα) = 81.15 cm^{-1}, $D_c = 1.973$ g cm^{-3}, $D_m = 1.99$ (2) g cm^{-3}, $F(000)$ = 520, space group $P\bar{1}$. An absorption correction was applied

on the basis of the indexed crystal faces (100), ($\bar{1}00$), ($1\bar{1}0$), ($\bar{1}10$), (101), and ($\bar{1}0\bar{1}$) and direction cosines calculated for the PW 1100 data. Maximum and minimum values of transmission factors were 0.5370 and 0.2701, respectively. The total number of reflections measured to 2θ(Mo Kα) = 60° for a crystal of dimensions ca. 0.11 $\times$ 0.16 $\times$ 0.16 mm (optimum size 0.25 mm) was 5630; of these no reflections were rejected as being systematically absent or having zero F or I and 290 were multiple observations ($R = 0.036$), leaving 5340 unique reflections of which 2659 obeyed the condition $I \geq 3\sigma(I)$. Seven very weak reflections were considered as poorly calculating and were omitted during refinement. Thus, 2652 reflections were used in the final refinement.

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 $R = 0.088$ [(py)$_3$COH complex] and 0.072 [(py)$_2$(N-MeIm)COH 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 $R = 0.055$ and 0.052 and $R' = 0.051$ and 0.048 (for observed reflections), where $R' = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o|$. Since only some of the hydrogen atoms were observed in the difference Fourier syntheses with the exception of a hydroxyl hydrogen, hydrogen atom coordinates were calculated according to the geometry of the carbon atom to which they are bonded (C–H = 1.08 Å) and all hydrogen atoms were assigned isotropic thermal parameters. A reasonable position (peak height intensity 0.70 e Å^{-3} above background) was observed in the difference synthesis for the hydroxyl hydrogen in the (py)$_3$COH complex, and this position was refined. No peak corresponding to a reasonable position for the hydroxyl hydrogen was observed for the (py)$_2$(N-MeIm)COH complex.

Final refinements with hydrogen atoms riding on their respective carbon atoms involved 241 [(py)$_3$COH complex] and 237 [(py)$_2$(N-MeIm)COH complex] variables and gave $R = 0.044$ and 0.042 and $R' = 0.040$ and 0.038, respectively. Final difference syntheses had no major characteristic greater than 1.15 [(py)$_3$COH complex] and 2.02 e Å^{-3} [(py)$_2$(N-MeIm)COH complex], these occurring in the vicinity of the mercury atom; the largest shift to esd ratios in the final cycles were 0.162 for the H(O) x parameter and 0.075 for the O x parameter [(py)$_3$COH] and 0.502 for the O U_{33} parameter [(py)$_2$-

(14) J. Hornstra and B. Stubbe, PW 1100 Data Processing Program, Philips Research Laboratories, Eindhoven, Holland.

Table III. Fractional Coordinates and Thermal Parameters ($\times 10^4$) for Mercury and ($\times 10^3$) for Other Nonhydrogen Atoms in [MeHg((py)$_2$(N-MeIm)COH)]NO$_3$

| atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	2198 (0)	337 (0)	3698 (0)	606 (3)	413 (2)	592 (2)	165 (2)	194 (2)	114 (1)
C(1)	99 (1)	167 (1)	402 (2)	99 (10)	88 (9)	172 (13)	57 (8)	63 (9)	53 (9)
C(2)	277 (1)	−247 (1)	602 (1)	38 (5)	45 (4)	30 (4)	−2 (4)	0 (4)	8 (4)
C(3)	307 (1)	−317 (1)	735 (1)	64 (6)	68 (6)	37 (5)	2 (5)	2 (4)	15 (4)
C(4)	288 (1)	−258 (1)	889 (1)	72 (7)	93 (8)	35 (5)	−20 (7)	−9 (5)	15 (5)
C(5)	241 (1)	−139 (1)	902 (1)	77 (8)	76 (7)	41 (6)	−9 (6)	6 (5)	−6 (5)
C(6)	213 (1)	−77 (1)	765 (1)	57 (6)	63 (6)	48 (5)	−2 (5)	14 (5)	−12 (5)
C(7)	289 (1)	−306 (1)	424 (1)	43 (5)	34 (4)	24 (4)	6 (4)	3 (3)	3 (3)
C(3')	536 (1)	−360 (1)	299 (1)	52 (6)	72 (7)	111 (9)	27 (6)	13 (6)	16 (6)
C(2')	375 (1)	−207 (1)	347 (1)	32 (4)	45 (4)	24 (4)	10 (4)	1 (3)	3 (3)
C(4')	525 (1)	−118 (1)	230 (1)	35 (5)	62 (6)	65 (6)	1 (5)	12 (4)	2 (5)
C(5')	456 (1)	−19 (1)	247 (1)	40 (5)	58 (5)	55 (5)	−10 (4)	11 (4)	11 (4)
C(2'')	168 (1)	−332 (1)	329 (1)	52 (5)	44 (4)	22 (4)	−2 (4)	5 (4)	−2 (3)
C(3'')	101 (1)	−459 (1)	333 (1)	63 (7)	62 (6)	64 (6)	−9 (6)	4 (6)	2 (5)
C(4'')	−8 (1)	−479 (1)	253 (1)	67 (9)	93 (9)	77 (8)	−22 (7)	0 (7)	−9 (7)
C(5'')	−49 (1)	−379 (2)	167 (1)	50 (7)	124 (10)	47 (6)	−19 (8)	−7 (5)	−10 (7)
C(6'')	20 (1)	−254 (1)	171 (1)	42 (6)	108 (9)	44 (5)	13 (6)	−5 (5)	11 (5)
N(1)	229 (1)	−130 (1)	615 (1)	48 (4)	54 (4)	33 (4)	2 (4)	9 (3)	−2 (3)
N(2)	317 (1)	312 (1)	123 (1)	58 (5)	48 (5)	70 (6)	1 (4)	13 (5)	2 (5)
N(3')	475 (1)	−235 (1)	293 (1)	43 (4)	53 (4)	43 (4)	10 (4)	5 (3)	1 (3)
N(1')	362 (1)	−75 (1)	321 (1)	44 (4)	41 (4)	39 (4)	8 (3)	3 (3)	2 (3)
N(1'')	128 (1)	−229 (1)	250 (1)	45 (5)	63 (5)	40 (4)	5 (4)	−2 (3)	10 (4)
O	331 (1)	−435 (1)	436 (1)	67 (4)	40 (3)	60 (4)	17 (3)	11 (3)	12 (3)
O(1)	278 (1)	212 (1)	24 (1)	98 (6)	74 (5)	104 (6)	3 (5)	17 (5)	−34 (5)
O(2)	373 (1)	296 (1)	251 (1)	142 (9)	86 (6)	118 (7)	−7 (6)	−32 (7)	32 (6)
O(3)	296 (1)	430 (1)	104 (1)	116 (7)	52 (5)	117 (6)	17 (5)	−33 (5)	−2 (4)

(N-MeIm)COH, unrealistic as H(O) not located] and 0.109 for the C(3') U_{13} parameter [(py)$_2$(N-MeIm)COH].

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.

The atomic scattering factors for neutral atoms[15] were corrected for anomalous dispersion.[16] All calculations were carried out with the Monash University B6700 computer; the major programs used were SHELX-76,[17] ORFFE,[18] and MEANPL.[19] Figures were drawn with use of ORTEP.[20]

Results

The new ligand bis(2-pyridyl)methane [(py)$_2$CHPh], required for ^{1}H NMR studies (see below), was prepared by reaction of 2-benzylpyridyllithium with 2-bromopyridine

$$\text{2-benzylpyridine} \xrightarrow[\text{(ii) 2-Br(py)}]{\text{(i) PhLi}} \text{(py)}_2\text{CHPh}$$
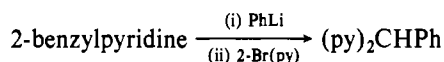
and the complexes were isolated from addition reactions in acetone

$$\text{MeHgNO}_3 + \text{L} \rightarrow [\text{MeHgL}]\text{NO}_3$$
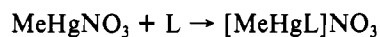
Structures of Complexes in Solution. For complexes [MeHgL]NO$_3$ with polydentate ligands containing pyridyl and imidazolyl rings a ^{1}H NMR method allows determination of coordination behavior of the ligands. The method, described in detail elsewhere,[7] is based on two approaches. (1) For complexes containing an uncoordinated ring in the 2 position of pyridine or N-methylimidazole the chemical shift of the MeHg^{II} proton occurs upfield from that of similar complexes
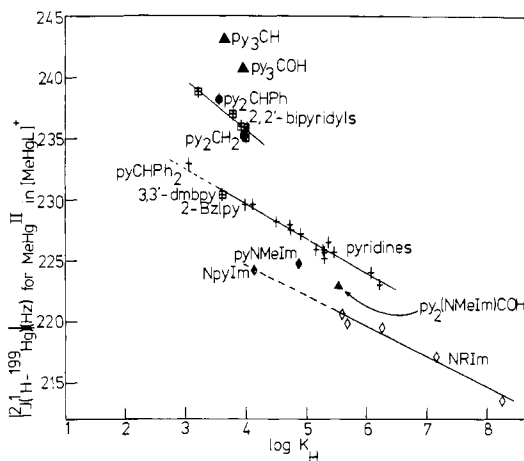

Figure 1. $|^2J(^1\text{H}-^{199}\text{Hg})|$ for [MeHgL]NO$_3$ (in CD$_3$OD) vs. log K_H for the ligands (L). log K_H values are those obtained for a 50% dioxane–water mixture as solvent: (+) L = pyridines; (□) L = 2,2'-bipyridyls; (◊) L = N-alkylimidazoles. Values of $^2J(^1\text{H}-^{199}\text{Hg})$ for new complexes are given in Table I; the appropriate ligands have log K_H 3.04 [(py)CHPh$_2$], 3.54 [(py)$_2$CHPh], 3.98 [(py)$_3$COH], and 5.53 [(py)$_2$(N-MeIm)COH]. Values of $^2J(^1\text{H}-^{199}\text{Hg})$ and log K_H are given elsewhere for other complexes.[4,7,9]

without an uncoordinated ring. Increased shielding results from ring current anisotropy, and from structural determinations of complexes with pyridyl donors it appears that orientation of the rings to effect this shielding results from a weak π interaction between mercury and the ring.[21,22] (2) Comparison of $^2J(^1\text{H}-^{199}\text{Hg})$ with values for closely related unidentate ligands shows that chelation results in higher values for the coupling constant. For example, Figure 1 indicates that in a plot of $^2J(^1\text{H}-^{199}\text{Hg})$ vs. log K_H (of LH$^+$) complexes of 2,2'-bipyridyls have $^2J(^1\text{H}-^{199}\text{Hg})$ ca. 6 Hz higher than for unidentate pyridines of similar log K_H; the complexes of 2-

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(20) C. K. Johnson, "ORTEP, a Fortran Ellipsoid Plot Program for Crystal Structure Illustration", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn.

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(22) A. J. Canty, N. Chaichit, and B. M. Gatehouse, *Acta Crystallogr., Sect. B*, **B36**, 786 (1980).
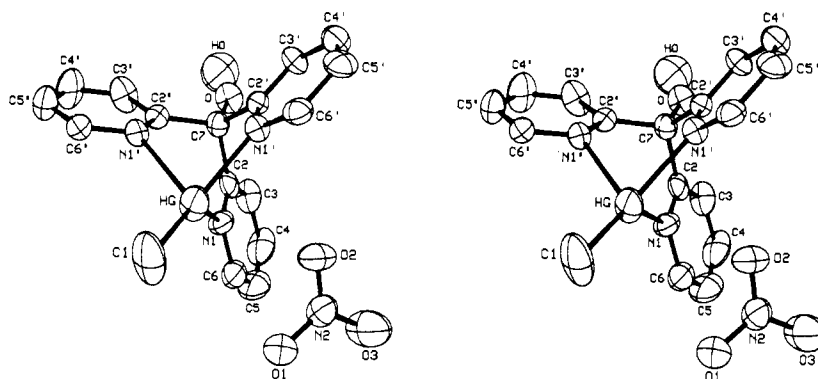
Figure 2. Structure of the cation [MeHg((py)$_3$COH)]$^+$ showing the relationship between Hg and the nearest nitrate ion.

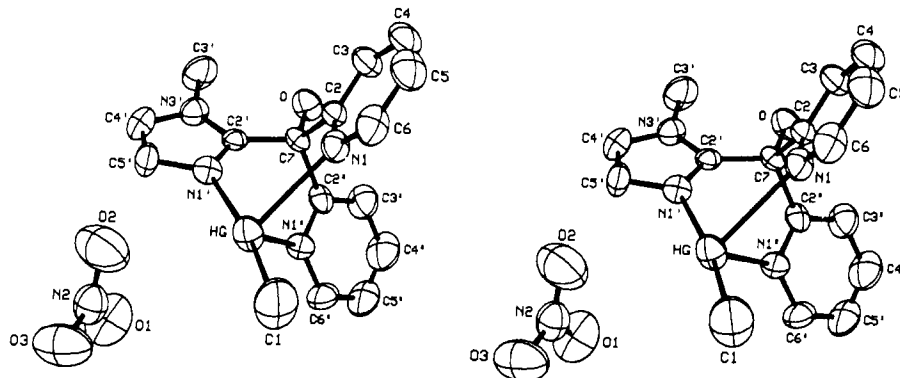**Figure 3.** Structure of the cation [MeHg((py)$_2$(*N*-MeIm)COH)]$^+$ showing the relationship between Hg and the nearest nitrate ion.

benzylpyridine (2-Bzlpy)[22] and unidentate[21] 3,3'-dimethyl-2,2'-bipyridyl (3,3'-dmbpy) have $^2J(^1H-^{199}Hg)$ appropriate for unidentate pyridines, and they have δ(MeHg) 0.17–0.42 ppm upfield from complexes of pyridines that do not have aromatic groups in the 2 position.

An additional factor, requiring consideration for complexes of tripod ligands, is the observation that for complexes of (py)$_2$CR$_2$ (R = Me, Et) δ(MeHg) occurs 0.17–0.46 ppm upfield from unidentate pyridines—indicating unidentate coordination—but $^2J(^1H-^{199}Hg)$ is ca. 4 Hz higher than for unidentate pyridines of similar log K_H.[7] In these cases it has been established[7] that the higher coupling constants result from steric interaction between mercury and the bulky "CR$_2$py" group; e.g., the complex with unidentate (py)CMe$_2$Ph has $^2J(^1H-^{199}Hg)$ similar to that of unidentate (py)$_2$CMe$_2$. However, for (py)$_3$CH [and presumably (py)$_3$COH and (py)$_2$(*N*-MeIm)COH] it appears that a steric effect is absent as the (py)CHPh$_2$ complex has $J(^1H-^{199}Hg)$ as expected for a simple pyridine complex (see below) (Figure 1).

The complex [MeHg((py)$_3$CH)]NO$_3$ has a $^2J(^1H-^{199}Hg)$ of 243.1 Hz, higher than that for complexes of pyridines and bidentate (py)$_2$CH$_2$ (235.4 Hz), and the MeHg^{II} proton resonance (−2.43 ppm) is not shifted upfield from values for unidentate pyridines (−2.47 to −2.68 ppm), consistent with presence of (py)$_3$CH as a tridentate ligand.[7] Spectra of (py)CHPh$_2$ and (py)$_2$CHPh complexes support assignment of tridentate behavior for (py)$_3$CH. The ligand (py)CHPh$_2$ is a model for "unidentate (py)$_3$CH" as the "CHPh$_2$" group is expected to have identical steric effect to "CH(py)$_2$" in "unidentate (py)$_3$CH", and (py)$_2$CHPh is similarly a model for "bidentate (py)$_3$CH". The complex with (py)CHPh$_2$ has $^2J(^1H-^{199}Hg)$ appropriate for a unidentate (Figure 1), and δ(MeHg) is 0.16–0.47 ppm upfield from unidentate pyridine complexes lacking aryl groups in the 2 position. The complex with bidentate (py)$_2$CHPh has $^2J(^1H-^{199}Hg)$ intermediate between that of (py)CHPh$_2$ and (py)$_3$CH (Figure 1), consistent with tridentate behavior for (py)$_3$CH, and has δ(MeHg)

0.65 ppm upfield from that of the (py)$_3$CH complex indicating that the third pyridyl group in the (py)$_3$CH complex is not in the same orientation as the phenyl group in the (py)$_2$CHPh complex and is thus most likely coordinated to mercury.

The complex [MeHg((py)$_3$COH)]NO$_3$ has $^2J(^1H-^{199}Hg)$ = 240.7 Hz (Figure 1) and δ(MeHg) = −2.69 ppm (cf. −2.47 to −2.68 for unidentate pyridines without aromatic substituents in the 2 position), consistent with tridentate coordination in solution. This complex has tridentate (py)$_3$COH in the solid state (see below).

For [MeHg((py)$_2$(*N*-MeIm)COH)]NO$_3$ the ligand is not present as a tridentate in methanol as the MeHg^{II} ^{1}H resonance, at −2.89 ppm, occurs 0.2 ppm upfield from the complex with tridentate (py)$_3$COH. For the ambidentate ligand VII

NpyIm
VII

py-NMeIm
VIII
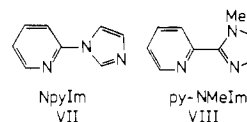
the MeHg^{II} complex has $^2J(^1H-^{199}Hg)$ appropriate for binding to the imidazolyl nitrogen (Figure 1);[7] for the bidentate ligand VIII $^2J(^1H-^{199}Hg)$ for the MeHg^{II} complex is ca. 2.5 Hz above the $^2J(^1H-^{199}Hg)$, log K_H line for unidentate N-substituted imidazolyl ligands (Figure 1),[7] and consistent with bidentate coordination by (py)$_2$(*N*-MeIm)COH (IX) $^2J(^1H-^{199}Hg)$ for

[MeHg(py)$_2$(NMeIm)COH)]$^+$
in methanol
IX
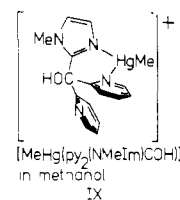
its MeHg^{II} complex is 2.1 Hz higher than expected for coordination as a unidentate via the imidazolyl ring.

Table IV. Interatomic Distances (Å) and Angles (Deg) in [MeHg((py)₃COH)]NO₃

(a) Mercury Environment

Hg-C(1)	2.03 (2)	Hg-N(1')	2.28 (1)	Hg···O(2)	2.97 (1)
Hg-N(1)	2.45 (1)	Hg-N(1'')	2.53 (1)		
C(1)-Hg-N(1)	132 (1)	N(1)-Hg-N(1')	76 (0)	N(1')-Hg-N(1'')	75 (0)
C(1)-Hg-N(1')	150 (1)	N(1)-Hg-N(1'')	76 (0)	N(1')-Hg-O(2)	75 (0)
C(1)-Hg-N(1'')	119 (1)	N(1)-Hg-O(2)	78 (0)	N(1'')-Hg-O(2)	144 (0)
C(1)-Hg-O(2)	97 (1)				

(b) (py)₃COH Group

C(2)-N(1)	1.34 (2)	C(2')-N(1')	1.34 (2)	C(2'')-N(1'')	1.32 (2)
C(2)-C(3)	1.40 (1)	C(2')-C(3')	1.38 (2)	C(2'')-C(3'')	1.40 (2)
C(3)-C(4)	1.41 (2)	C(3')-C(4')	1.39 (2)	C(3'')-C(4'')	1.38 (2)
C(4)-C(5)	1.36 (4)	C(4')-C(5')	1.36 (2)	C(4'')-C(5'')	1.37 (3)
C(5)-C(6)	1.38 (2)	C(5')-C(6')	1.40 (2)	C(5'')-C(6'')	1.36 (2)
C(6)-N(1)	1.35 (2)	C(6')-N(1')	1.33 (2)	C(6'')-N(1'')	1.36 (1)
C(2)-C(7)	1.55 (2)	C(2')-C(7)	1.57 (2)	C(2'')-C(7)	1.54 (1)
C(2)-N(1)-Hg	125 (1)	C(2')-N(1')-Hg	128 (1)	C(2'')-N(1'')-Hg	122 (1)
C(6)-N(1)-Hg	116 (1)	C(6')-N(1')-Hg	114 (1)	C(6'')-N(1'')-Hg	117 (1)
C(2)-N(1)-C(6)	118 (1)	C(2')-N(1')-C(6')	119 (1)	C(2'')-N(1'')-C(6'')	119 (1)
N(1)-C(2)-C(3)	123 (1)	N(1')-C(2')-C(3')	123 (1)	N(1'')-C(2'')-C(3'')	121 (1)
N(1)-C(2)-C(7)	118 (1)	N(1')-C(2')-C(7)	119 (1)	N(1'')-C(2'')-C(7)	118 (1)
C(3)-C(2)-C(7)	119 (1)	C(3')-C(2')-C(7)	119 (1)	C(3'')-C(2'')-C(7)	121 (1)
C(2)-C(3)-C(4)	117 (2)	C(2')-C(3')-C(4')	118 (1)	C(2'')-C(3'')-C(4'')	118 (2)
C(3)-C(4)-C(5)	119 (1)	C(3')-C(4')-C(5')	121 (1)	C(3'')-C(4'')-C(5'')	120 (1)
C(4)-C(5)-C(6)	120 (2)	C(4')-C(5')-C(6')	118 (1)	C(4'')-C(5'')-C(6'')	118 (1)
N(1)-C(6)-C(5)	122 (2)	N(1')-C(6')-C(5')	123 (1)	N(1'')-C(6'')-C(5'')	123 (1)
C(7)-O	1.41 (2)	O-H(O)	0.72 (22)		
C(2)-C(7)-C(2')	109 (1)	C(2)-C(7)-O	106 (1)	C(2'')-C(7)-O	110 (1)
C(2)-C(7)-C(2'')	110 (1)	C(2')-C(7)-O	109 (1)	C(7)-O-H(O)	125 (15)
C(2')-C(7)-C(2'')	113 (1)				
O(1)ᵃ-H(O)	2.08 (18)	O···O(1)ᵃ	2.75 (2)	O···O(3)ᵃ	3.29 (2)
O(3)ᵃ-H(O)	2.81 (24)				
O-H(O)···O(1)ᵃ	156 (19)	O-H(O)···O(3)ᵃ	127 (16)		

(c) Nitrate Ion

N(2)-O(1)	1.26 (2)	N(2)-O(2)	1.21 (2)	N(2)-O(3)	1.22 (1)
O(1)-N(2)-O(2)	122 (1)	O(1)-N(2)-O(3)	118 (1)	O(2)-N(2)-O(3)	120 (1)

ᵃ Symmetry code: x̄, ȳ, 1 − z.

Crystallographic Studies of [MeHgL]NO₃ [L = (py)₃COH, (py)₂(N-MeIm)COH].

Aspects of the molecular geometry of these complexes are given in Tables IV and V, and both structures are composed of [MeHgL]⁺ cations and regular (within 3σ) nitrate ions. Pyridyl and imidazolyl rings are planar (within 2σ) (Tables IX and X).[23] The MeHgᴵᴵ group has Hg-C(1) = 2.03 (2) [(py)₃COH] and 2.05 (1) Å [(py)₂(N-MeIm)COH], within the range observed for other MeHgᴵᴵ complexes containing pyridyl donor groups [1.95 (4)-2.10 (2) Å].[5-8,21,22,24]

Both ligands are present as tridentates, and the coordination geometry for mercury is irregular; viz., the complexes have angles N-Hg-N = 75-76 (0) [(py)₃COH] and 71-78 (0)° [(py)₂(N-MeIm)COH], but a wide range of angles C-Hg-N and distances Hg-N: 119-150 (1)°, 2.28-2.53 (1) Å [(py)₃COH]; 110-170 (0)°, 2.13-2.71 (1) Å [(py)₂(N-MeIm)COH]. For both structures mercury is more strongly bonded to one nitrogen (N1') [Hg-N1' = 2.28 (1) [(py)₃COH] and 2.13 (1) Å [(py)₂(N-MeIm)COH]] than to the other two (N1, N1'') [2.45 (1), 2.53 (1) [(py)₃COH] and 2.66 (1), 2.71 (1) Å [(py)₂(N-MeIm)COH]]. The shortest mercury-nitrogen bond forms the largest angle with the MeHgᴵᴵ group: C(1)-Hg-N(1') = 150 (1) [(py)₃COH] and 170 (0)° [(py)₂(N-MeIm)COH]. A similar trend occurs for the Et₃terpy complex (Table VI), and as in the Et₃terpy complex, the MeHgᴵᴵ group is much closer to the plane of the ring containing N(1') than to the plane containing N(1) or

N(1''), reflecting weaker mercury-nitrogen bonding with the latter donor atoms.

In [MeHg((py)₃COH)]NO₃ the mercury atom interacts weakly with a nitrate oxygen at 2.97 (1) Å, within the sum of van der Waals radii (3.13 Å),[25] and in both complexes the hydroxyl group may be hydrogen bonded to a nearby nitrate ion as oxygen···oxygen distances occur in the range 2.75 (2)-3.29 (2) Å (Tables IV and V).

Discussion

In methanol (py)₂CHPh and (py)₂(N-MeIm)COH act as bidentates, with an additional weak Hg···π interaction involving the phenyl and one uncoordinated pyridyl ring, respectively, indicated from ¹H NMR spectra. This coordination behavior is similar to that observed in the solid state for the L-tyrosine complex [p-OHPhCH₂CH(NH₂)CO₂]HgMe, which has a bidentate amino acid group and a weak π interaction,[29] with the aromatic ring in a similar orientation to that found for the phenyl ring in the 2-benzylpyridine complex.[22] For the L-tyrosine complex ¹H NMR spectra are also consistent with

(23) Supplementary material.
(24) R. T. C. Brownlee, A. J. Canty, and M. F. Mackay, *Aust. J. Chem.* **31**, 1933 (1978).
(25) With use of O = 1.4 Å,[26] N = 1.5 Å,[26] and Grdenič's[27] upper limit of 1.73 Å for the radius of mercury. 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.[28]
(26) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p 260.
(27) D. Grdenič, *Q. Rev., Chem. Soc.*, **19**, 303 (1965).
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(29) N. W. Alcock, P. A. Lampe, and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1324 (1978).

Table V. Interatomic Distances (Å) and Angles (Deg) in [MeHg((py)$_2$(N-MeIm)COH)]NO$_3$

(a) Mercury Environment^a

Hg–C(1)	2.05 (1)	Hg–N(1')	2.13 (1)	Hg–N(1'')	2.71 (1)
Hg–N(1)	2.66 (1)				
C(1)–Hg–N(1)	110 (0)	N(1)–Hg–N(1')	78 (0)	N(1')–Hg–N(1'')	74 (0)
C(1)–Hg–N(1')	170 (0)	N(1)–Hg–N(1'')	71 (0)	N(1')–Hg–O(2)	84 (0)
C(1)–Hg–N(1'')	114 (0)	N(1)–Hg–O(2)	138 (0)	N(1'')–Hg–O(2)	138 (0)
C(1)–Hg–O(2)	86 (0)				

(b) (py)$_2$(N-MeIm)COH Group

C(2')–N(1')	1.34 (1)	C(2)–N(1)	1.32 (1)	C(2'')–N(1'')	1.34 (1)
C(2')–C(3')	1.35 (1)	C(2)–C(3)	1.37 (1)	C(2'')–C(3'')	1.38 (1)
C(3')–N(3')	1.49 (1)	C(3)–C(4)	1.39 (1)	C(3'')–C(4'')	1.36 (2)
C(4')–N(3')	1.37 (1)	C(4)–C(5)	1.34 (2)	C(4'')–C(5'')	1.35 (2)
C(4')–C(5')	1.33 (1)	C(5)–C(6)	1.35 (1)	C(5'')–C(6'')	1.37 (2)
C(5')–N(1')	1.38 (1)	C(6)–N(1)	1.33 (1)	C(6'')–N(1'')	1.35 (1)
C(2')–C(7)	1.52 (1)	C(2)–C(7)	1.55 (1)	C(2'')–C(7)	1.54 (1)
C(2')–N(1')–Hg	127 (1)	C(2)–N(1)–Hg	121 (0)	C(2'')–N(1'')–Hg	116 (0)
C(5')–N(1')–Hg	124 (1)	C(6)–N(1)–Hg	118 (1)	C(6'')–N(1'')–Hg	120 (1)
C(2')–N(1')–C(5')	109 (1)	C(2)–N(1)–C(6)	118 (1)	C(2'')–N(1'')–C(6'')	118 (1)
N(1')–C(2')–N(3')	108 (1)	N(1)–C(2)–C(3)	123 (1)	N(1'')–C(2'')–C(3'')	121 (1)
C(7)–C(2')–N(1')	125 (1)	N(1)–C(2)–C(7)	116 (1)	N(1'')–C(2'')–C(7)	120 (1)
C(7)–C(2')–N(3')	127 (1)	C(3)–C(2)–C(7)	121 (1)	C(3'')–C(2'')–C(7)	119 (1)
C(2')–N(3')–C(4')	108 (1)	C(2)–C(3)–C(4)	117 (1)	C(2'')–C(3'')–C(4'')	119 (1)
C(3')–N(3')–C(2')	131 (1)	C(3)–C(4)–C(5)	120 (1)	C(3'')–C(4'')–C(5'')	121 (1)
C(4')–N(3')–C(3')	120 (1)	C(4)–C(5)–C(6)	120 (1)	C(4'')–C(5'')–C(6'')	118 (1)
C(5')–C(4')–N(3')	108 (1)	N(1)–C(6)–C(5)	122 (2)	N(1'')–C(6'')–C(5'')	123 (1)
C(4')–C(5')–N(1')	107 (1)				
C(7)–O	1.40 (1)				
C(2)–C(7)–C(2')	110 (1)	C(2')–C(7)–C(2'')	114 (1)	C(2')–C(7)–O	110 (1)
C(2)–C(7)–C(2'')	107 (1)	C(2)–C(7)–O	107 (1)	C(2'')–C(7)–O	109 (1)
O···O(2)^b	3.03 (1)	O···O(3)^b	2.89 (1)		

(c) Nitrate Ion

N(2)–O(1)	1.23 (1)	N(2)–O(2)	1.21 (1)	N(2)–O(3)	1.22 (1)
O(1)–N(2)–O(2)	121 (1)	O(1)–N(2)–O(3)	122 (1)	O(2)–N(2)–O(3)	117 (1)

^{a} The nearest oxygen atom to mercury is O(2) of the nitrate ion at 3.21 (1) Å. ^{b} Symmetry code: $x, y - 1, z$.

Table VI. Selected Structural Data for Complexes [MeHgL]NO$_3$ with Tridentate Nitrogen Donor Ligands

L	Hg–C(1), Å	C(1)–Hg–N(1'), deg	Hg–N(1'), Å	Hg···plane', Å	Hg–N(1), Å	Hg···plane, Å	Hg–N(1''), Å	Hg···plane'', Å	Hg···O, Å
Et$_3$terpy^a	2.06 (3)	171 (1)	2.26 (2)	−0.121 (1)	2.51 (2)	−0.886 (1)	2.61 (2)	−1.032 (1)	2.78 (2)
(py)$_3$COH	2.03 (2)	150 (1)	2.28 (1)	−0.054 (1)	2.45 (1)	0.349 (1)	2.53 (1)	0.590 (1)	2.97 (1)
(py)$_2$(N-MeIm)COH	2.05 (1)	170 (0)	2.13 (1)	0.075 (0)	2.66 (1)	−0.612 (0)	2.71 (1)	−1.136 (0)	3.21 (1)

^{a} Et$_3$terpy = 4,4'4''-triethyl-2,2':6',2''-terpyridyl.[7]

the presence of a weak π interaction in solution.[29]

In the solid state both (py)$_3$COH and (py)$_2$(N-MeIm)COH complexes have irregular coordination geometry, with all mercury–nitrogen interactions at least 0.5 Å less than the sum of van der Waals radii,[25] and the largest distortion (from tetrahedral) occurs for the (py)$_2$(N-MeIm)COH complex. Both complexes have coordination geometry quite different from the approximately planar geometry found for [MeHg-(Et$_3$terpy)]NO$_3$.[7] The mercury environment in the (py)$_2$(N-MeIm)COH complex resembles a trigonal bipyramid lacking one equatorial donor (Figure 3), with angles around mercury 10–24° from ideal values. This geometry, compared with that for [MeHg((py)$_3$COH)]NO$_2$, is consistent with stronger binding of imidazolyl than pyridyl rings and is in accord with solution studies showing that N-methylimidazole forms a complex [MeHgL]$^+$ of higher stability constant (log K = 6.96)[3] than that for pyridine (4.8,[30] 4.72[31]).

It is of interest to compare coordination geometries in the solid state with coordination behavior of the ligands in methanol, even though relationships between these may not be strictly valid, e.g., length of the weakest mercury–nitrogen interaction with bidentate or tridentate coordination in solution;

even for ligands remaining fully chelated on dissolution the coordination geometry may be altered. However, consistent with tridentate behavior by (py)$_3$CX (X = H, OH) in methanol, but bidentate coordination by Et$_3$terpy and (py)$_2$(N-MeIm)COH, the Hg–N(1'') interaction is longer in the Et$_3$terpy and (py)$_2$(N-MeIm)COH complexes and the mercury atom is further removed from the ligand plane containing N(1'') (Table VI).

Several factors appear to be relevant to these observations: (1) involvement of all 6p orbitals of mercury for (py)$_3$CX compared with two for Et$_3$terpy; (2) shorter Hg–N(1) and –N(1'') bonds in the (py)$_3$COH complex compared with those in the Et$_3$terpy complex, possibly resulting from (1); (3) greater basicity of the N-MeIm ring in (py)$_2$(N-MeIm)COH, resulting in formation of a more dominant C(1)–Hg–N(1') moiety, compared with (py)$_3$COH, resulting in weaker Hg–pyridyl ring [N(1),N(1'')] bonding.

None of the tridentate ligands studied act as unidentates in solution, consistent with the observation[4,7,8] that all bidentate ligands studied by X-ray crystallography [2,2'-bipyridyl,[5] (py)$_2$CH$_2$,[7] N-(2-pyridyl)pyrazole,[8] and bis(N-pyrazolyl)-methane ((pz)$_2$CH$_2$)[8]] remain bidentate on dissolution of their MeHg^{II} complexes, even though one of these complexes [(pz)$_2$CH$_2$] has the weaker Hg–N interaction [2.96 (2) Å] longer than for the tridentate ligands.

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Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and the Department of Radiology, Harvard Medical School and Brigham and Women's Hospital, Boston, Massachusetts 02115

New 2,2'-Bipyridine and 1,10-Phenanthroline Oxohalide Complexes of Technetium(VII) and -(V)

ALAN DAVISON,*[1a] ALUN G. JONES,[1b] and MICHAEL J. ABRAMS[1a]

Novel complexes of heptavalent technetium with the formualtion TcO$_3$XL (L = 2,2'-bipyridine, X = Cl, Br; L = 1,10-phenanthroline, X = Cl) have been prepared and characterized by elemental analysis and optical and vibrational spectroscopy. These complexes can be reduced to the pentavalent species, TcOX$_3$L, by heating in ethanolic aqueous HX. TcOX$_3$ (2,2'-bipyridine) (X = Cl, Br) can be synthesized independently from n-Bu$_4$NTcOX$_4$ and 2,2'-bipyridine in ethanolic aqueous HX.

Introduction

One of the basic differences between the chemistry of technetium and that of rhenium is that, under similar conditions, technetium is easier to reduce than rhenium.[2,3] For example, the interaction of ReO$_4^-$ with phosphines in ethanolic HCl yields complexes of stoichiometry ReOCl$_3$(PR$_3$)$_2$. Under similar conditions, TcO$_4^-$ reacts to give the complexes *trans*-TcCl$_4$(PR$_3$)$_2$ and *mer*-TcCl$_3$(PR$_3$)$_3$.[4] Also, in contrast to rhenium, technetium does not, as yet, have a well-developed chemistry in the heptavalent oxidation state.

We now report the preparation of 2,2'-bipyridine and 1,10-phenanthroline oxohalide technetium(VII) complexes from NH$_4$TcO$_4$ and the respective ligands in ethanolic aqueous haloacids. These complexes, unlike the known rhenium analogue ReO$_3$Cl(bpy), are readily reduced to oxohalide technetium(V) species.

Experimental Section

Technetium as NH$_4$^{99}TcO$_4$ was obtained as a gift from New England Nuclear (NEN), Billerica, MA. All manipulations were carried out in laboratories approved for low-level radioactivity (^{99}Tc is a weak β emitter with a half-life of 2.12 × 10^5 years and particle energy of 0.292 MeV). All precautions followed have been detailed elsewhere.[5,6] Rhenium, as NaReO$_4$, was obtained from Cleveland Refractory Metals, Solon, OH.

Infrared spectra were recorded in the range 4000–300 cm^{-1} on a Perkin-Elmer PE180 grating infrared spectrophotometer as KBr pellets. Optical spectra, in solution, were measured with a Cary 17 spectrophotometer. Raman spectra were obtained as solid samples using a Spex Ramalog with the 5145-Å line of an Ar laser. ^{1}H NMR measurements were made on a Jeol FX-90Q 90-MHz spectrometer with acetone-d_6 as solvent and Me$_4$Si as the internal calibrant.

Conductivity measurements were performed in acetonitrile with use of a Yellow Springs Model 3403 conductivity cell and a Beckman RC-16C conductivity bridge. Melting points were obtained with a Mel-Temp apparatus and are uncorrected.

Prior to use, distilled water was passed through a Barnstead Ultrapure D8902 cartridge, followed by redistillation in a Corning AG-1 water still. The ligands, 2,2'-bipyridine (bpy) and 1,10-phenanthroline hydrate (phen), were obtained from the J. T. Baker Chemical Co., Phillipsburg, NJ. n-Bu$_4$NTcOCl$_4$ and n-Bu$_4$NTcOBr$_4$ were prepared by literature methods.[6,7] Absolute ethanol was used throughout. All other chemicals were used without further purification unless otherwise specified. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Preparation of the Complexes. Trioxochloro(2,2'-bipyridine)-technetium(VII). To a 50-mL round-bottom flask were added a stirbar, EtOH (10 mL), and 0.70 mL of 0.379 M NH$_4$TcO$_4$ (0.26 mmol). To the stirred solution was added 0.30 g of bpy (1.97 mmol) dissolved in EtOH (10 mL), followed by the dropwise addition of 12 N HCl (2 mL). Within 10 min a bright yellow solid precipitated. This solid was isolated by suction filtration, washed with acetone (3 × 15 mL), and dried in vacuo. The yield of TcO$_3$Cl(bpy) was 0.07 g (0.21 mmol), 81% based on Tc; mp 162 °C dec. This material is insoluble in toluene, ethanol, methanol, and slightly soluble in acetone, methylene chloride, and acetonitrile. In water, the complex hydrolyzes back to TcO$_4^-$.

Anal. Calcd for C$_{10}$H$_8$ClN$_2$O$_3$Tc: C, 35.46; H, 2.39; Cl, 10.47; N, 8.27. Found: C, 35.61; H, 2.11; Cl, 10.49; N, 8.29. Optical spectrum in (CH$_3$CN): 298 nm (ϵ 1.9 × 10^4 L mol^{-1} cm^{-1}), 310 (sh). IR spectrum (KBr): $\nu_{Tc=O}$, 905 (s), 885 (s), 865 (m) cm^{-1}. Raman spectrum: $\nu_{Tc=O}$, 882 (m), 902 (s) cm^{-1}.

Trioxochloro(1,10-phenanthroline)technetium(VII). This complex was prepared as a yellow solid in 75% yield by the above procedure using phen (6:1 excess over TcO$_4^-$). It solubility is similar to TcO$_3$Cl(bpy); mp 205 °C dec. Anal. Calcd for C$_{12}$H$_8$ClN$_2$O$_3$Tc: C, 39.74; H, 2.23; Cl, 9.77; N, 7.73. Found: C, 40.14; H, 2.26; Cl, 9.81; N, 7.74. Optical spectrum in CH$_3$CN: 269 (3.7 × 10^4). IR (KBr): $\nu_{Tc=O}$ 895 (s), 885 (s), 870 (m) cm^{-1}. Raman spectrum: $\nu_{Tc=O}$, 898 (vs) cm^{-1}.

Trioxobromo(2,2'-bipyridine)technetium(VII). This complex was prepared similarly to TcO$_3$Cl(bpy) by using HBr (48%) instead of 12 N HCl. It was washed with 4 N HBr after filtration, followed by acetone and dried in vacuo. The yellow orange solid was obtained

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