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one edge. About Ag(2) the angle between peripheral bromines Br(2)-Ag-Br(1) ($x, y - 1, z$) is enlarged to 116.7 (2)°, while that subtending the shared edge to Ag(3), Br(3)-Ag(2)-Br(4) ($x, y - 1, z$) is dimished (100.8 (2)°). Among the bond lengths, only slight differences are found about Ag(3) (2.718 (4), 2.735 (7) Å), with greater differences about Ag(1) (range 2.699 (4)-2.745 (4) A) and considerable differences about Ag(2) (2.667 (6)-2.739 (7) Å). Interestingly, silver···silver distances are more compact than in $(Ag_2I_3)_n^{n-}$ where Ag···Ag across the polymer is 3.045 (9) and longitudinally 3.697 (9) Å; the corresponding distances in the present polymer are 3.476 (9) and 3.172 (4) Å with the shortest Ag···Ag distance occurring in the *iodide*. The cation geometries (Table III) are consistent with the proposed $MeCOHNHCMe_3$ cation, presumably arising out of a prolonged high-temperature reaction of methyl and *tert*-butyl cyanide and traces of moisture remaining in the freshly precipitated silver cyanide. The C-C-O-NC skeletons are planar (σ (least-squares plane), 0.014, 0.011, 0.021 Å) in consequence of amide conjugation, also evident in the geometries. O(H) nearest-neighbor contacts are consistent with reasonable and anticipated hydrogen-bonding expectations (O(1)···O(2) ($x + 1/2, y + 1/2, z$), 2.41 (2) Å; O(3)···O(3) ($1^1/_2 - x, ^1/_2 - y, z$), 2.35 (3) Å).

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Registry No. $(C_6H_{14}NO)_3[Ag_5Br_8]$, 92219-58-4.

Supplementary Material Available: Listings of thermal and hydrogen parameters and structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of Methylmercury(II) with Flexible Tripod Ligands Containing Pyridyl and *N*-Methylimidazolyl Groups, Including the Crystal Structure of [Bis(*N*-methylimidazol-2-yl)(pyridin-2-yl)methanol-*N*,*N'*,*N''*]methylmercury(II) Nitrate, $[MeHg(py(N\text{-}MeIm)_2COH)]NO_3$

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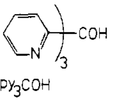
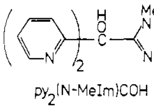
In its complexes with tripod ligands containing pyridine and *N*-methylimidazole groups studied crystallographically, $[MeHgL]NO_3$ (L = $(py)_3COH$, $(py)_2(N\text{-}MeIm)COH$),[3] the


py_3COH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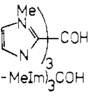
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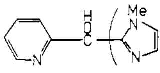
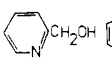
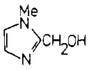

$py(N\text{-}MeIm)_2COH$

ligands are present as tridentates. The complexes have one strong Hg-N coordination interaction and two weaker Hg···N interactions. However, in the $(N\text{-}MeIm)_3COH$ complex, $MeHg^{II}$ is bound to one *N*-MeIm group and weakly to the hydroxy group, with two *N*-MeIm groups uncoordinated.[4]

We report here the crystal structure determination for $[MeHg(py(N\text{-}MeIm)_2COH)]NO_3$, completing the series of complexes involving $(py)_n(N\text{-}MeIm)_{3-n}COH$ (n = 0-3). The synthesis and spectroscopic study of $[MeHgL]NO_3$ (L = $pyCH_2OH$, $N\text{-}MeImCH_2OH$, $pyzCH_2OH$) are also reported, as the first two of these are model ligands closely related to the tripod ligands.


$pyCH_2OH$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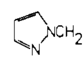
$pyzCH_2OH$

Experimental Section

Reagents. Methylmercuric nitrate,[5] $py(N\text{-}MeIm)_2COH$,[6] $pyzCH_2OH$,[7] and $N\text{-}MeImCH_2OH$[8] were prepared and purified as described, and $pyCH_2OH$ (Fluka) was distilled under reduced pressure.

Preparation of Complexes. The complex $[MeHg(py(N\text{-}MeIm)_2COH)]NO_3$ was prepared as described,[4] and for the new complexes equimolar quantities of $MeHg^{II}$ nitrate and ligand in acetone gave microcrystalline $[MeHg(pyCH_2OH)]NO_3$ immediately (yield 81%) and microcrystalline $[MeHg(pyzCH_2OH)]NO_3$ (41%) and $[MeHg(N\text{-}MeImCH_2OH)]NO_3$ (92%) formed on slow evaporation over several days. Characterization data for the new complexes are summarized in Table I. Microanalyses were by the Australian Microanalytical Service.

Physical Measurements. ^1H NMR spectra at 100 MHz were measured on a JEOL JNM-4H-100 spectrometer. Chemical shifts 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 (pK_a of LH^+) were measured in 50% dioxane-water following an experimental procedure given earlier.[9-11]

Crystallography

Crystal Data: $C_{15}H_{16}HgN_6O_4$, M_r = 544.9, monoclinic, space group $P2_1/n$ (C^5_{2h}, No. 14, variant), a = 15.786 (4) Å, b = 15.065 (3) Å, c = 7.715 (2) Å, β = 91.24 (2)°, V = 1834.2 (8) Å^3, D_{measd} = 1.95 (1) g cm^{-3}, D_{calcd} (Z = 4) = 1.97 g cm^{-3}, $F(000)$ = 1040, monochromatic Mo Kα radiation, λ = 0.7106_9 Å, μ_{Mo} = 81 cm^{-1}. Specimen: pseudospherical polyhedron, maximum and minimum diameters 0.30 and 0.25 mm, approximately as Syntex sphere 0.28 mm in diameter for absorption correction, A^*_{min}, A^*_{max} = 3.31, 4.82; T = 295 K.

Structure Determination. A unique data set was measured within the limit $2\theta_{max}$ = 45° on a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta-\theta$ scan mode; 2510 independent reflections were measured, 1798 with $I > 3\sigma(I)$ being considered observed and used in the six-block least-squares refinement. Anisotropic thermal parameters were refined for the non-hydrogen atoms; hydrogen atoms were included at calculated positions (x, y, z, U_{iso}) and constrained. Residuals on $|F|$ at convergence were 0.051, 0.060 (R, R'), reflection weights being $(\sigma^2(F_o) + 0.0007(F_o)^2)^{-1}$. Neutral complex scattering factors were used;[12] computation used the X-RAY 76 program system[13] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Atom numbering is shown in the molecular projection; fractional coordinates for non-hydrogen atoms are given in Table II, and interatomic distances and angles, in Table III.

Unusual Features. High thermal motion on the nitrate ion may

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Table I. Characterization Data for the Complexes[a]

complex	% calcd (% found) C	H	Hg	δ(MeHg)[b]	$\lvert{}^2J({}^1\mathrm{H}\text{–}{}^{199}\mathrm{Hg})\rvert$,	δ(other protons)[b,c]
$[\mathrm{MeHg(pyCH_2OH)}]\mathrm{NO_3}$	21.7 (22.1)	2.6 (2.4)	51.9 (52.0)	−2.60	231.9[d]	4.13 m ($H_{3,5}$), 4.55 m (H_4), 5.07 m (H_6)
$[\mathrm{MeHg}(N\text{-}\mathrm{MeImCH_2OH})]\mathrm{NO_3}$	18.5 (18.6)	2.8 (3.0)	51.5 (51.7)	−2.66	218.1[e]	3.51 d, 3.67 d ($H_{4,5}$),[f] 0.05 (*N*-Me)
$[\mathrm{MeHg(pyzCH_2OH)}]\mathrm{NO_3}$	16.0 (15.5)	2.4 (2.2)	53.4 (53.8)	−2.62	228.6[g]	3.10 t (H_4),[h] 4.42 m ($H_{3,5}$)[h]

[a] Solutions in CD_3OD. [b] Chemical shifts from internal 1,4-dioxane (3.64 ppm from Me_4Si); integrations appropriate for formula presented. [c] CH_2 occurs with OH at δ 1–1.4. [d] Expected value, from a ${}^2J({}^1\mathrm{H}\text{–}{}^{199}\mathrm{Hg})$ vs. $\log K_\mathrm{H}$ relationship where $\log K_\mathrm{H} = 4.03$ (1) for $pyCH_2OH$ in 1:1 dioxane–water at 229.7 Hz. [e] Expected value 218.9 Hz, where $\log K_\mathrm{H} = 6.28$ (1) for *N*-$MeImCH_2OH$. [f] $J_{4,5} = 1.7$ Hz. [g] Expected value 230.9 Hz, where $\log K_\mathrm{H} = 1.91$ (3) for $pyzCH_2OH$. [h] $J_{4,5} \sim J_{3,4} \sim 2.4$ Hz.

Table II. Fractional Coordinates (×10^4) for Non-Hydrogen Atoms in $[\mathrm{MeHg(py}(N\text{-}\mathrm{MeIm})_2\mathrm{COH)}]\mathrm{NO_3}$

atom	*x*/*a*	*y*/*b*	*z*/*c*
Hg	1240.7 (4)	4050.3 (4)	2781.0 (8)
C(1)	953 (13)	5357 (11)	3365 (29)
C(2)	673 (7)	2317 (8)	5064 (15)
C(3)	−441 (10)	1422 (12)	6680 (20)
C(4)	412 (9)	2701 (10)	7714 (17)
C(5)	1000 (11)	3219 (10)	7048 (20)
C(7)	569 (7)	1833 (8)	3317 (15)
C(2′)	1292 (8)	2019 (9)	2110 (16)
C(3′)	1418 (12)	462 (11)	795 (19)
C(4′)	2233 (9)	1824 (11)	92 (18)
C(5′)	2254 (9)	2685 (11)	539 (20)
C(2″)	−258 (7)	2162 (8)	2427 (15)
C(3″)	−911 (9)	1600 (9)	1949 (18)
C(4″)	−1612 (9)	1953 (11)	1135 (19)
C(5″)	−1658 (9)	2855 (12)	857 (18)
C(6″)	−979 (10)	3358 (10)	1401 (19)
N(1)	1178 (6)	2984 (7)	5389 (13)
N(2)	2182 (8)	86 (8)	6007 (19)
N(3)	193 (7)	2120 (7)	6434 (13)
N(1′)	1646 (6)	2803 (8)	1831 (14)
N(3′)	1643 (7)	1400 (7)	1065 (14)
N(1″)	−294 (6)	3042 (7)	2179 (3)
O	489 (5)	910 (5)	3601 (11)
O(1)	1554 (8)	533 (8)	6299 (15)
O(2)	2275 (11)	−186 (13)	4599 (19)
O(3)	2678 (8)	−67 (8)	7214 (17)

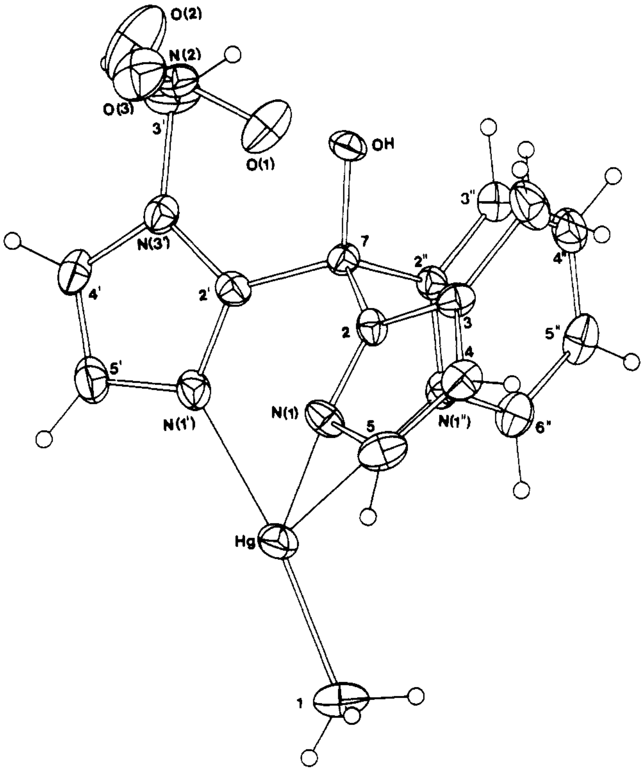

Figure 1. Projection of the cation and neighboring anion, showing atom labeling; 20% thermal ellipsoids given for the non-hydrogen atoms. Hydrogen atoms have an arbitrary radius of 0.1 Å.

indicate slight disorder, probably accounting for the rather restricted range of accessible data.

Results

The complexes of $pyCH_2OH$, *N*-$MeImCH_2OH$, and $pyzCH_2OH$ have appropriate microanalyses and ^1H NMR spectra (Table I). In particular, the complexes have ${}^2J({}^1\mathrm{H}\text{–}{}^{199}\mathrm{Hg})$ for the $\mathrm{MeHg^{II}}$ group within ca. 2 Hz of values expected for presence of these ligands on the basis of the relationship[11]

$${}^2J({}^1\mathrm{H}\text{–}{}^{199}\mathrm{Hg}) = -a \log K_\mathrm{H} + b$$

for pyridines ($a = 2.96$, $b = 241.6$), N-substituted imidazoles (2.50, 234.6), and N-substituted pyrazoles (2.64, 235.9). Several attempts to grow crystals, from water or methanol, gave crystalline products unsuitable for single-crystal diffraction studies.

The structure of the cation $[\mathrm{MeHg(py}(N\text{-}\mathrm{MeIm})_2\mathrm{COH)}]^+$ in its nitrate salt is shown in Figure 1, and aspects of the molecular geometry are given in Tables III and IV. The pyridine and *N*-methylimidazole rings are planar,[14] and the

Table III. Interatomic Distances (Å) and Angles (deg) in $[\mathrm{MeHg(py}(N\text{-}\mathrm{MeIm})_2\mathrm{COH)}]\mathrm{NO_3}$

(a) Mercury Environment[a]

Hg-C(1)	2.07 (2)	Hg-N(1′)	2.12 (1)
Hg-N(1)	2.58 (1)	Hg-N(1″)	2.89 (1)
C(1)-Hg-N(1)	114.2 (6)	N(1)-Hg-N(1′)	74.6 (4)
C(1)-Hg-N(1′)	170.5 (7)	N(1)-Hg-N(1″)	75.6 (3)
C(1)-Hg-N(1″)	110.3 (6)	N(1′)-Hg-N(1″)	74.7 (3)

(b) py(*N*-MeIm)$_2$COH Group[b]

C(2′)-N(1′)-Hg	127.0 (8)	C(2)-N(1)-Hg	111.3 (8)	C(2″)-N(1″)-Hg	117.7 (7)
C(5′)-N(1′)-Hg	124.8 (9)	C(5)-N(1)-Hg	125.7 (9)	C(6″)-N(1″)-Hg	124.2 (9)
C(7)-O	1.41 (1)				
C(2)-C(7)-C(2′)	112.6 (10)	C(2′)-C(7)-C(2″)	107.9 (9)	C(2′)-C(7)-O	110.4 (10)
C(2)-C(7)-C(2″)	108.1 (9)	C(2)-C(7)-O	109.8 (9)	C(2″)-C(7)-O	107.9 (9)

(c) Nitrate Ion

N(2)-O(1)	1.22 (2)	N(2)-O(2)	1.17 (2)	N(2)-O(3)	1.23 (2)
O(1)-N(2)-O(2)	119 (2)	O(1)-N(2)-O(3)	118 (1)	O(2)-N(2)-O(3)	123 (2)

[a] The nearest oxygen atom to mercury is O(2) [$\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$] of the nitrate ion at 3.22 (2) Å. [b] Complete details of the ligand geometry are given in Table VIII (supplementary material).

Table IV. Selected Structural Data for Complexes $[\mathrm{MeHgL}]\mathrm{NO_3}$, Where L = $(\mathrm{py})_n(N\text{-MeIm})_{3-n}\mathrm{COH}$ (n = 0–3)

	dominant C(1)-Hg-N(1′) moiety				secondary Hg···N and/or Hg···O interactions				
L	Hg-C(1)	C(1)-Hg-N(1′)	Hg-N(1′)	Hg···plane′	Hg-N(1)	Hg···plane	Hg-N(1″)	Hg···plane″	Hg···O
$(N\text{-MeIm})_3\mathrm{COH}$[a]	2.05 (1)	176.1 (5)	2.125 (7)	0.07					2.680 (6)[b]
$\mathrm{py}(N\text{-MeIm})_2\mathrm{COH}$	2.07 (2)	170.5 (7)	2.12 (1)	−0.304	2.58 (1)	−1.589	2.89 (1)	−0.456	
$(\mathrm{py})_2(N\text{-MeIm})\mathrm{COH}$[c]	2.05 (1)	170 (1)	2.13 (1)	0.075	2.66 (1)	−0.612	2.71 (1)	−1.136	3.21 (1)[d]
$(\mathrm{py})_3\mathrm{COH}$[c]	2.03 (2)	150 (1)	2.28 (1)	−0.054	2.45 (1)	0.349	2.53 (1)	0.590	2.97 (1)[d]

[a] From ref 4. [b] Oxygen atom of the OH group of $(N\text{-MeIm})_3\mathrm{COH}$. [c] From ref 3. [d] Oxygen atom of a nitrate ion.

nitrate ion is regular (within 3σ in bond lengths and angles), with the mercury atom 3.22 (2) Å from the nearest nitrate oxygen, corresponding closely to the value expected[15] for a van der Waals contact. As the ring geometries do not deviate from expected values, only the most important aspects of ligand geometry are presented in Table III.

The ligand is present as a tridentate, based on one strong Hg–N(1′) (N-MeIm) bond, 2.12 (1) Å, and two weak Hg···N interactions of 2.58 (1) Å (N-MeIm) and 2.89 (1) Å (py). As expected for the presence of weak Hg···N interactions, the C(1)–Hg–N(1′) angle is not far removed from linearity, 170.5 (7)°, with the Hg···N interactions opposite this angle. Although the weak interactions are well short of van der Waals contact (ca. 3.23 Å),[15] they are clearly weak since the mercury atom lies 1.589 Å above the mean plane of the N-MeIm ring and 0.456 Å above the mean plane of the pyridine ring, compared with 0.304 Å for the strongly bound N-MeIm ring (Table IV).

Although the hydroxyl hydrogen could not be confidently located, a close contact is observed to the nitrate ion, O(H)···O(1) being 2.71 (1) Å; no other O···O distances <3.2 Å were observed.

Discussion

A comparison of the coordination geometries for mercury in the complexes of $(\mathrm{py})_n(N\text{-MeIm})_{3-n}\mathrm{COH}$ (n = 0–3) is given in Table IV.

The complex with $(N\text{-MeIm})_3\mathrm{COH}$ has an almost linear C(1)–Hg–N(1′) group, 176.1 (5)°, a weak Hg···OH interaction, 2.680 (6) Å, and two uncoordinated N-MeIm groups. Presence of uncoordinated groups in this complex illustrate that the ligands are flexible in their coordination behavior and, thus, do not constrain mercury to adopt high coordination geometries. The flexibility of these ligands is also shown in $[\mathrm{Me_2Au(py)_3CH}]\mathrm{NO_3}\cdot 2\mathrm{H_2O}$, where the closely related ligand $(\mathrm{py})_3\mathrm{CH}$ is present as a bidentate.[16]

For the other complexes involving $(\mathrm{py})_n(N\text{-MeIm})_{3-n}\mathrm{COH}$ (n = 1–3), all three rings are involved in interactions with mercury and the hydroxy group is uncoordinated.

For complexes containing both N-MeIm and py groups, i.e. complexes with $(\mathrm{py})_2(N\text{-MeIm})\mathrm{COH}$ and $\mathrm{py}(N\text{-MeIm})_2\mathrm{COH}$, a clear preference for binding of Hg to N-MeIm groups is apparent, with Hg–N(1′)(N-MeIm) similar to that of the $(N\text{-MeIm})_3\mathrm{COH}$ complex and with secondary Hg···N interactions 2.58 (1)–2.89 (1) Å. These two complexes have C(1)–Hg–N(1′) about 10° removed from linearity, and all three N-MeIm complexes have Hg–N(1′) similar to that in complexes of related unidentate nitrogen donor ligands, e.g., 2.12 (2) Å in $[\mathrm{MeHg(py)}]\mathrm{NO_3}$.[17]

The complex with $(\mathrm{py})_3\mathrm{COH}$ is somewhat different from those with $(\mathrm{py})_2(N\text{-MeIm})\mathrm{COH}$ and $\mathrm{py}(N\text{-MeIm})_2\mathrm{COH}$ and is even further removed from the geometry of the $(N\text{-MeIm})_3\mathrm{COH}$ complex. In the $(\mathrm{py})_3\mathrm{COH}$ complex the strongest Hg-N interaction, 2.28 (1) Å, is longer than in the other complexes and forms an angle C(1)–Hg–N(1′), 150 (1)°, with a much larger deviation from linearity. The weaker Hg-N(1′) bond and smaller C(1)–Hg–N(1′) angle presumably reflect presence of stronger secondary Hg···N interactions, 2.45 (1) and 2.53 (1) Å, which are significantly shorter than in the other complexes, 2.66 (1)–2.89 (1) Å.

Stronger secondary interactions in $[\mathrm{MeHg((py)_3COH)}]\mathrm{NO_3}$ than in the other complexes may result from the higher basicity of N-MeIm groups than py groups, giving a "MeHg(N-MeIm)" moiety in complexes of $(\mathrm{py})_n(N\text{-MeIm})_{3-n}\mathrm{COH}$ (n = 0–2) having a lower Lewis acidity than "MeHg(py)" in the $(\mathrm{py})_3\mathrm{COH}$ complex. However, in contrast with $(\mathrm{py})_3\mathrm{COH}$, the complex with the related bidentate ligand $(\mathrm{py})_2\mathrm{CH_2}$ has C–Hg–N, 172 (1)°, and a weak Hg···N′ interaction, 2.75 (2) Å, although this complex also exhibits an appreciable Hg···$\mathrm{ONO_2}$ interaction, 2.76 (2) Å.[10]

The group of complexes involving flexible polydentate ligands $(\mathrm{py})_n(N\text{-MeIm})_{3-n}\mathrm{COH}$ (n = 0–3) clearly demonstrate that the mercury atom in MeHg[11] can adopt coordination geometries higher than linear, with the geometries at mercury indicating the presence of two strong bonds (C–Hg–N) with additional weaker interactions. Similar features are found for related nitrogen donor bidentate ligands[4,10,18,19] and the planar tridentate 2,2′:6′,2″-terpyridyl.[10] Unlike linear complex ions, e.g. $[\mathrm{MeHg(py)}]^+$, or regular coordination geometries, in for example some halomercurates $\mathrm{HgX_3}^-$ and $\mathrm{HgX_4}^{2-}$, an sp^n hybridization scheme as an approximate description for the bonding in the mercury coordination sphere does not appear to be applicable. Although secondary interactions are weak, they do appear to be appreciable in most of the complexes, and, with an approximately linear C–Hg–N geometry as the dominant bonding feature, it is proposed that the mercury atom is essentially sp hybridized (with different s and p character involved in bonding to carbon and nitrogen), with the weaker bonds involving interactions of ligand lone pairs (or π orbitals in the case of Hg···phenyl interactions)[20,21] with the other 6p orbitals of mercury.

In addition to their proposed application as model ligands for the environment of metal ions in some biological systems, particularly zinc in carbonic anhydrase,[22] the flexible tripod ligands $(\mathrm{py})_n(N\text{-MeIm})_{3-n}\mathrm{COH}$ (n = 0–3) clearly have applications in probing the coordination behavior or organometallic cations.

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(14) Supplementary material.

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Registry No. [MeHg(pyCH$_2$OH)]NO$_3$, 92056-02-5; [MeHg(*N*-MeImCH$_2$OH)]NO$_3$, 92056-04-7; [MeHg(pyzCH$_2$OH)]NO$_3$, 92056-06-9; [MeHg(py(*N*-MeIm)$_2$COH)]NO$_3$, 88993-39-9.

Supplementary Material Available: Listings of H atom fractional coordinates (except for the hydroxyl hydrogen), thermal parameters, least-squares planes, interatomic distances and angles including detailed ligand geometry, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Fast Infrared Detection of $Cr(CO)_5N_2$ in Room-Temperature Solution

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The generation of dinitrogen-substituted transition-metal carbonyl complexes of the general formula $M(CO)_x(N_2)$ has been largely restricted to low-temperature conditions. $Ni(CO)_3N_2$[1,2] and $Cr(CO)_5N_2$[3] have been synthesized at 10–20 K by the use of matrix isolation methods and more recently by employing pressurized liquid noble gases[4,5] at low temperature as solvents. $Ni(CO)_3N_2$ was found to be thermally unstable at 112 K[4] while $Cr(CO)_5N_2$ was reported to be stable up to 238 K,[5b] the upper limit of the available temperature range. On the other hand, $M(CO)_xN_2$ complexes have scarcely been reported in room-temperature solutions. Conventional flash photolysis studies have implicated $Cr(CO)_5N_2$ as a possible transient in the solution photochemistry of $Cr(CO)_6$ in hydrocarbon[6] and perfluoro solvents[7] containing dinitrogen. In both cases a transient absorption at 370 nm was assigned to $Cr(CO)_5N_2$, consistent with the low-temperature data.[3,5b]

We have previously shown[8] how, at room temperature, flash photolysis with infrared detection can give important information not accessible from the UV–visible counterpart. In addition to kinetic data, valuable structural information can be gained from the frequency and intensity of the infrared bands associated with a particular transient. With regard to transition metal carbonyls the CO stretching region is often a direct reflection of the geometry of the molecule itself.

The photochemistry of $Cr(CO)_6$ is still not fully understood,[9] but CO detachment is known to occur with the resultant formation of a highly reactive $Cr(CO)_5$ species. This coordinatively unsaturated molecule will readily react with numerous ligands to form $Cr(CO)_5L$ derivatives either as labile species[8,10] or as stable products.[11]

Table I. Transient Infrared Absorptions (cm^{-1}) of $Cr(CO)_5N_2$ at Various Temperatures and in Various Media

		absorptions and assignments				
medium	*T*, K	$\nu_e(CO)$	$\nu_{a_1}(CO)$	$\nu_{a_1}(NN)$	^{13}CO satellite	ref
cyclohexane	~293[a]	1976[b]	1966,[b] 2086[c]	2240[d]	1946[c]	this work[e]
liquid xenon	194	1975.5	1966.8, 2087.0	2237.2		ref 5
CH_4/N_2 matrix	20	1978.2	1959.5,[f] 2086[f]	2240.6[f]		ref 3

[a] Room temperature. [b] Slit width 0.5 mm. [c] Slit width 1.25 mm. [d] Slit width 5 mm. [e] Reproducibility ±2 cm^{-1} or better. [f] Raman band.

Using our technique of flash photolysis with infrared detection,[8] we have now studied the reaction of $Cr(CO)_5$ with dinitrogen, and we report on the identification and behavior of $Cr(CO)_5N_2$ in cyclohexane solution at room temperature.

Experimental Section

The instrumental design of the flash photolysis with infrared detection setup has been described previously.[8] In this study the HgCdTe detector was used throughout. A xenon flash lamp (Xenon Corp., 50 J/pulse, 90% discharge within 5 μs) was used as the exciting light source. The lamp and the associated power supply were securely housed in copper shielding to prevent electromagnetic interference from the flash.

Materials. $Cr(CO)_6$ was purchased from Merck (z. S.) and N_2 (99.9995%) from L'Air Liquide. Cyclohexane (Merck, z. A.) was distilled under argon in a column of 3-m length and 25-mm internal diameter filled with Wilson spirals of 2-mm diameter (80–100 theoretical plates); its purity was checked by gas chromatography and UV spectroscopy. Impurity peaks detectable by gas chromatography were <0.2 ppm. $Cr(CO)_5(^{13}CO)$ was prepared from the thermal reaction of (η^2-*cis*-cyclooctene)$Cr(CO)_5$ with ^{13}CO and identified by mass and infrared spectroscopy.[12]

Sample Preparation. We have previously been concerned[8] that flushing solutions even with high-purity gases could over a period of time accumulate impurities. The sampling equipment was therefore modified according to suggestions by Kelly et al.[7,10] A glass vessel, prefilled with N_2, fitted with greaseless taps was used to hold the sample solution. The solvent, cyclohexane, was vacuum degassed prior to the addition of $Cr(CO)_6$. The solution was then degassed by pumping at room temperature, and N_2 gas was added to a pressure of slightly more than 1 atm. The solution was then shaken to ensure saturation with the gas. In this way volatile impurities should be removed, and continuous purging with gas (a possible source for accumulating impurities) was avoided.

In all experiments 10^{-3} M solutions of $Cr(CO)_6$ were used. It was found that it was not necessary to exclude daylight in order to obtain reproducible kinetic and spectral data.

The infrared cell (path length 1 mm) used in these experiments was also evacuable. Circular CaF_2 windows were pressed into a metal casing by indium gaskets, and the cell was connected to the solution vessel by stainless-steel capillary tubing. Thus the entire system was completely closed, and there was no need to flush solutions with gas or to purge the infrared cell. A fresh solution was introduced, normally after about four flashes, into the infrared cell by means of a magnetic solenoid valve. A test series of 16 flashes without changing the solution showed only minimal loss of transient signal.

Results and Discussion

So far, in no flash photolysis study of $Cr(CO)_6$ in cyclohexane has a species been observed prior to the formation of the ubiquitous solvent complex, $Cr(CO)_5C_6H_{12}$. Indeed, it has been shown that this species is already formed within 25 ps of excitation of $Cr(CO)_6$.[13] Not surprisingly, therefore, when a 10^{-3} M solution of $Cr(CO)_6$ in cyclohexane saturated with

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