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Quadruple Coordination of the Carbonyl Oxygen Atom of an Amide by a Cyclic Tetradentate Lewis Acid

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Treatment of oxo[μ-(3,4,5,6-tetramethyl-1,2-phenylene)]dimercury (**6**) with trifluoromethanesulfonic acid produces the bis(trifluoromethanesulfonate) salt of cyclic compound **7**, in which two 1,2-phenylenedimercury units are bridged by hydroxyl groups. μ-Hydroxide **7** is a tetradentate Lewis acid, and it forms a novel 1:2 complex with diethylformamide. An X-ray crystallographic study established that μ-hydroxide **7** defines an approximately planar and symmetric 10-membered ring, which holds four Lewis acidic atoms of mercury in an orientation that allows them to interact simultaneously with each of the two carbonyl oxygen atoms of the bound molecules of diethylformamide. Formation of the complex causes an important decrease in the carbonyl stretching frequency of the amide, which suggests that multiple coordination may weaken the C=O bond and enhance its reactivity. Treatment of dichloro(3,4,5,6-tetramethyl-1,2-phenylene)dimercury (**9**) with 2 equiv of $AgOSO_2CF_3$, followed by crystallization of the product from diethylformamide, provided a 2:1 complex of diethylformamide with the corresponding 1,2-phenylenedimercury bis(trifluoromethanesulfonate) **8**. An X-ray crystallographic study revealed that the complex is unusual because each Lewis acidic atom of mercury forms one of its two primary bonds to the formally neutral carbonyl oxygen atom of diethylformamide, and the anionic trifluoromethanesulfonate ligands are relegated to secondary bridging positions. Structural and spectroscopic effects suggest that binding of diethylformamide by bis(trifluoromethanesulfonate) **8** is unusually strong, even though it is monodentate.

Introduction

The study of the recognition and binding of Lewis bases by multidentate Lewis acids is an increasingly active area of research,[3−9] and it promises to yield discoveries of both fundamental and practical value as the special features of the coordination chemistry of multidentate Lewis acids become more fully understood. In earlier work in this field, we have shown that derivatives of 1,2-phenylenedimercury hold two Lewis acidic atoms of mercury in an orientation that permits them to interact simultaneously with single basic atoms in guest molecules.[3−7] For example, dichloride **1** forms a 1:1 complex with dimethylformamide in which the carbonyl oxygen atom of the guest is bound by both

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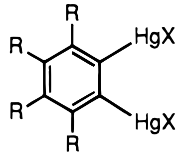
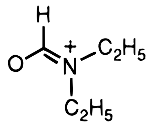
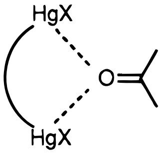
Lewis acidic sites of the host in the manner suggested by structure **2**.[4] The related bis(trifluoroacetate) **3**, a stronger bidentate Lewis acid, forms 2:3 complexes with amides in which two of the guests are doubly coordinated in the manner of adduct **2**; however, the carbonyl oxygen atom of the third amide is simultaneously bound by four Lewis acidic atoms of mercury provided by two molecules of host **3**, thereby creating the remarkable termolecular adduct **4**.[5] This observation suggests that it should be possible to link two 1,2-phenylenedimercury units to create rings containing four Lewis acidic atoms of mercury suitably arranged for the quadruple coordination of carbonyl compounds in the manner suggested by bimolecular structure **5**. In this paper, we show how this goal can be achieved.[10]



1 (R = H, X = Cl)
3 (R = CH_3, X = $OOCCF_3$)
8 (R = CH_3, X = OSO_2CF_3)
9 (R = CH_3, X = Cl)
10 (R = CH_3, X =





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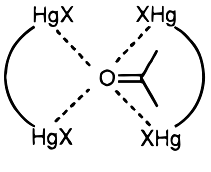

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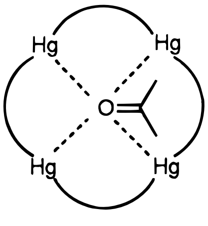

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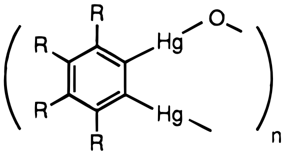
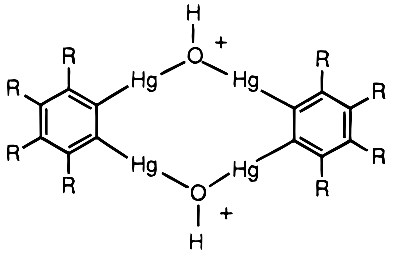


6 (R = CH_3)



7 (R = CH_3)

Results and Discussion

Treatment of oligomeric oxide **6**[6] with an equimolar amount of trifluoromethanesulfonic acid in ether, followed by crystallization of the product from diethylformamide, gave a 53% yield of a 2:1 complex of diethylformamide with the bis(trifluoromethanesulfonate) salt of cyclic μ-hydroxide **7**. The structure of the adduct was determined by X-ray crystallography, and the results are summarized in Figure 1 and in Tables 1 and 2. These data show that the four Lewis acidic atoms of mercury in μ-hydroxide **7** are oriented in an approximately planar and symmetric 10-membered ring. A remarkable feature of the structure is the binding of the two guest molecules of diethylformamide. The carbonyl oxygen atom of each interacts simultaneously and almost symmetrically with all four Lewis acidic atoms of mercury, creating the partial structure shown in Figure 1c. All four carbonyl O(11)···Hg distances are significantly shorter than the sum of the van der Waals radii of oxygen (1.40 Å)[11] and mercury (1.73 Å),[12] and the average distance (2.91(1) Å) is similar to the one measured for the quadruply coordinated amide in the 2:3 complex of bidentate bis(trifluoroacetate) **3** with diethylformamide (2.88(2) Å).[5] However, the four atoms of mercury that surround each carbonyl oxygen atom in the complex of cyclic μ-hydroxide **7** are more symmetrically disposed, and none lies close to the carbonyl plane. This observation is noteworthy because simple main-group Lewis acids normally favor $\eta^1(\sigma)$ coordination and lie near the carbonyl plane.[13]

In the structure of the complex of cyclic μ-hydroxide **7** with diethylformamide, atoms of mercury in adjacent 10-membered rings are bridged by trifluoromethanesulfonate, which also forms a hydrogen bond with O(1) (Figure 1b). Few other organomercuric trifluoromethanesulfonates are known,[14] and none of them have been characterized structurally,[15] despite the rapidly growing interest in trifluoromethanesulfonates of various metals.[16] The average Hg···O distance for interactions involving the trifluoromethanesulfonate group is 2.84(1) Å. Although the Hg···OSO_2CF_3 distances are all shorter than the sum of the van der Waals radii (3.13 Å),[11,12] they are nevertheless much longer than the average Hg–O bond length within the 10-membered ring (2.08(1) Å) and are similar to the average Hg···O

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[10] A preliminary account of this work has already appeared.[3]

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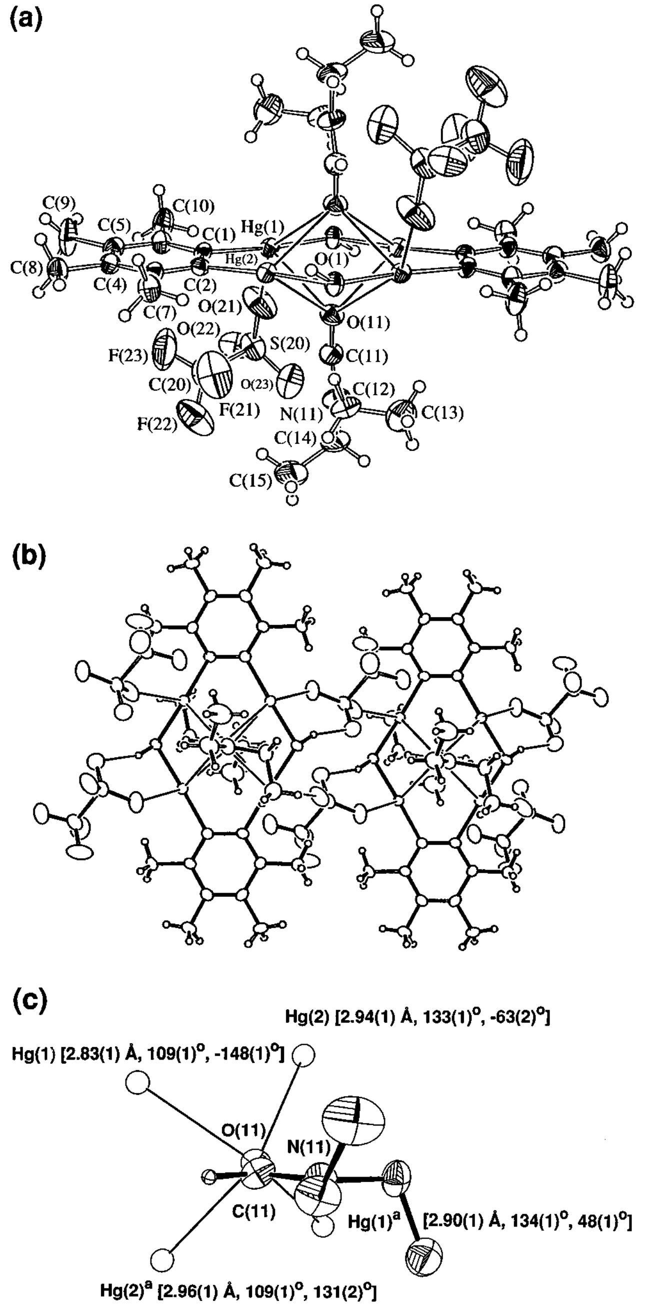

Figure 1. ORTEP views of the structure of the 2:1 complex of diethylformamide with the bis(trifluoromethanesulfonate) salt of cyclic μ-hydroxide **7**. (a) The atomic-numbering scheme. Non-hydrogen atoms are represented by ellipsoids corresponding to 50% probability, hydrogen atoms are shown as spheres of arbitrary size, and dative and ionic interactions with mercury are indicated using narrow lines. (b) Bridging and hydrogen bonding involving the trifluoromethanesulfonate ions. (c) One of the equivalent bound amides and the four associated atoms of mercury. The formyl hydrogen atom appears as a sphere of arbitrary size, while the other hydrogen atoms are omitted for simplicity. The three geometric parameters that appear next to each mercury atom correspond to the average carbonyl O(11)···Hg distances (Å)/C(11)–O(11)···Hg angles (deg)/N(11)–C(11)–O(11)···Hg dihedral angles (deg) for the bound amides.

Table 1. Selected Bond Lengths and Angles for the 2:1 Complex of Diethylformamide with Cyclic μ-Hydroxide 7

Bond Lengths (Å)			
Hg(1)–O(1)	2.08(1)	Hg(1)–O(21)	2.81(1)
Hg(2)–O(1)^a	2.08(1)	Hg(2)–O(22)^b	2.88(1)
Hg(1)–O(11)	2.83(1)	Hg(1)–C(1)	2.05(1)
Hg(2)–O(11)	2.94(1)	Hg(2)–C(2)	2.06(1)
Hg(1)–O(11)^a	2.96(1)	O(11)–C(11)	1.24(1)
Hg(2)–O(11)^a	2.90(1)	N(11)–C(11)	1.31(2)
Bond Angles (deg)			
O(1)–Hg(1)–O(11)	79.2(3)	C(1)–Hg(1)–O(11)^a	102.3(3)
O(1)–Hg(1)–O(11)^a	77.8(2)	C(2)–Hg(2)–O(11)^a	105.6(3)
O(1)^a–Hg(2)–O(11)	78.2(2)	C(1)–Hg(1)–O(21)	105.8(4)
O(1)^a–Hg(2)–O(11)^a	77.4(2)	C(2)–Hg(2)–O(22)^b	97.9(4)
O(1)–Hg(1)–O(21)	75.2(3)	C(11)–O(11)–Hg(1)	109.0(7)
O(1)^a–Hg(2)–O(22)^b	83.8(3)	C(11)–O(11)–Hg(2)	133.0(7)
O(1)–Hg(1)–C(1)	175.6(3)	C(11)–O(11)–Hg(1)^a	133.8(7)
O(1)^a–Hg(2)–C(2)	176.6(3)	C(11)–O(11)–Hg(2)^a	109.4(7)
C(1)–Hg(1)–O(11)	104.9(3)	Hg(1)–O(1)–Hg(2)^a	116.5(3)
C(2)–Hg(2)–O(11)	101.5(3)		

[a] $-x, 1-y, -z$. [b] $-1+x, y, z$.

Table 2. Crystallographic Data for the 2:1 Complex of Diethylformamide with Cyclic μ-Hydroxide 7

formula	$C_{32}H_{48}F_6Hg_4N_2O_{10}S_2$
fw	1601.21
cryst syst	monoclinic
space group	$P2_1/n$
cell constants	
a, Å	10.512(3)
b, Å	12.123(4)
c, Å	16.899(8)
β, deg	91.41(3)
cell volume, Å^3	2153(1)
Z	2
T, K	230
D_{calcd}, g cm^{-3}	2.470
μ $_{calcd}$, mm^{-1}	28.51
radiation (λ, Å)	graphite-monochromated Cu Kα (1.540 56)
cryst dimens, mm	0.19 × 0.21 × 0.40
scan width, deg	0.80 + 0.14 tan θ
$2\theta_{max}$, deg	140.0
data collcn range	$\pm h, \pm k, \pm l$
no. of reflns collcd	13 606
no. of reflns retained	3490
no. of params refined	253
goodness-of-fit	1.80
R_f	0.044
R_w	0.057
$\Delta\rho_{max}$, e Å^{-3}	2.18
$\Delta\rho_{min}$, e Å^{-3}	−2.94

distance involving datively bound diethylformamide (2.91(1) Å). This indicates that the Hg···O interactions involving trifluoromethanesulfonate are largely ionic, that the Hg–O bonds within the ring are largely covalent, and that dicationic structure **7** is a satisfactory representation of the fundamental molecular unit. Related salts of $(PhHg)_2OH^+$ are known, and their bond lengths and angles are similar to those of cyclic μ-hydroxide **7**.[17]

The carbonyl C(11)–O(11) bond length in each bound amide (1.24(1) Å) is somewhat longer than the generally accepted value for free tertiary amides (1.22 Å), and the N–C(O) bond length (1.31(2) Å) is slightly shorter than the normal value (1.35 Å).[18] The observed changes in

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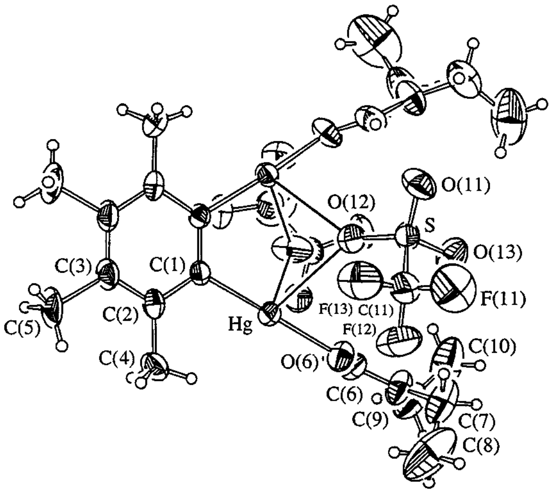

Figure 2. ORTEP view of the structure of the 2:1 complex of diethylformamide with phenylenedimercury bis(trifluoromethanesulfonate) **8**. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, hydrogen atoms are shown as spheres of arbitrary size, and ionic interactions with mercury are indicated using narrow lines.

Table 3. Selected Bond Lengths and Angles for the 2:1 Complex of Diethylformamide with Phenylenedimercury Bis(trifluoromethanesulfonate) 8

Bond Lengths (Å)	
Hg−O(6)	2.065(1)
Hg−C(1)	2.060(1)
Hg−O(11)[a]	2.89(1)
Hg−O(12)[b]	2.88(1)
Hg−O(12)[c]	2.81(1)
O(6)−C(6)	1.25(2)
N(6)−C(6)	1.29(2)
Bond Angles (deg)	
O(6)−Hg−O(11)[a]	76.8(4)
O(6)−Hg−O(12)[b]	79.4(4)
O(6)−Hg−O(12)[c]	87.8(4)
O(6)−Hg−C(1)	172.5(4)
C(1)−Hg−O(11)[a]	107.4(4)
C(1)−Hg−O(12)[b]	97.8(4)
C(1)−Hg−O(12)[c]	98.5(4)
Hg−O(6)−C(6)	122(1)

[a] $^1/_2 + x$, $^1/_2 - y$, $-^1/_2 + z$. [b] $1 + x, y, z$. [c] $1 - x$, y, $^3/_2 - z$.

Table 4. Crystallographic Data for the 2:1 Complex of Diethylformamide with Phenylenedimercury Bis(trifluoromethanesulfonate) 8

formula	$C_{22}H_{34}F_6Hg_2N_2O_8S_2$
fw	1033.80
cryst syst	monoclinic
space group	*C*2/*c*
cell constants	
a, Å	17.780(10)
b, Å	18.006(11)
c, Å	12.403(7)
β, deg	123.27(5)
cell volume, Å^3	3320(3)
Z	4
T, K	220
D_{calcd}, g cm^{-3}	2.068
μ_{calcd}, mm^{-1}	19.45
radiation (λ, Å)	graphite-monochromated Cu Kα (1.540 56)
cryst dimens, mm	0.26 × 0.42 × 0.58
scan width, deg	1.00 + 0.14 tan θ
$2\theta_{max}$, deg	140.0
data collcn range	$\pm h, \pm k, \pm l$
no. of reflns collcd	10 362
no. of reflns retained	2602
no. of params refined	190
goodness-of-fit	2.33
R_f	0.058
R_w	0.075
$\Delta\rho_{max}$, e Å^{-3}	3.07
$\Delta\rho_{min}$, e Å^{-3}	−1.77

bond lengths are consistent with weakening of the C=O bond, but they are not large enough to be considered crystallographically significant. However, the unusual bonding in the complex of diethylformamide with cyclic μ-hydroxide **7** causes an important shift in the carbonyl stretching frequency, which moves from 1689 cm^{-1} (Nujol) in free diethylformamide to 1648 cm^{-1} (Nujol) in the adduct. This shift is noteworthy because it suggests that multiple coordination may weaken the C=O bond and enhance its reactivity.

Bis(trifluoromethanesulfonate) **8** is an intriguing target for synthesis because it should be a stronger bidentate Lewis acid than the corresponding bis(trifluoroacetate) **3**. However, we were unable to make compound **8** directly by treating oligomeric oxide **6** with 2 equiv of trifluoromethanesulfonic acid. We therefore used an alternative approach starting from dichloride **9**, which was prepared in 73% yield by the reaction of bis(trifluoroacetate) **3** with HCl. Treatment of dichloride **9** with 2 equiv of $AgOSO_2CF_3$, followed by crystallization of the product from diethylformamide, then gave an 86% yield of a 2:1 complex of diethylformamide with bis(trifluoromethanesulfonate) **8**. The structure of the complex was determined by X-ray crystallography, and the results are summarized in Figure 2 and in Tables 3 and 4. The complex is very unusual because each atom of mercury forms one of its two essentially collinear primary bonds to the formally neutral carbonyl oxygen atom of diethylformamide rather than to one of the anionic trifluoromethanesulfonate ligands. The trifluoromethanesulfonates are relegated to secondary bridging positions, and the Hg⋯OSO_2CF_3 interactions lie in planes approximately perpendicular to the collinear primary bonds.[19] Comparison of the length of the Hg−O(6) bond to diethylformamide (2.06(1) Å) with the Hg⋯O(12) distance involving trifluoromethanesulfonate (2.88(1) Å) reveals that binding of the amides is largely covalent while that of the trifluoromethanesulfonates is largely ionic. As a result, hybrid **10** makes an important contribution to the structure of the adduct. Binding of the amides is therefore monodentate but nevertheless unusually strong, and the carbonyl C(6)−O(6) bond length (1.25(2) Å) and N−C(O) bond length (1.29(2) Å) are different from those in free amides.[18] As expected, this binding causes an important shift in the carbonyl stretching frequency of diethylformamide, which appears at 1643 cm^{-1} (KBr) in the adduct. The changes in bond lengths and stretching frequencies caused by monodentate binding to trifluoromethanesulfonate **8** are somewhat larger than those associated with tetradentate binding to μ-hydroxide **7**. This is principally because compound **8**, a mercuric trifluoromethanesulfonate, is intrinsically more Lewis acidic than compound **7**, a mercuric hydroxide.

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(19) For references, see: Kaupp, M.; von Schnering, H. G. *Inorg. Chem.* **1994**, *33*, 2555.

Conclusions

Our work has established that multidentate Lewis acids derived from 1,2-phenylenedimercury can bind the carbonyl oxygen atom of amides in unusual ways. In particular, two 1,2-phenylenedimercury units can be linked together to create cyclic *μ*-hydroxide **7**, which orients four Lewis acidic atoms of mercury in such a way that all can interact simultaneously with the carbonyl oxygen atom of diethylformamide. The resulting quadruple coordination is a dramatic illustration of the capacity of carbonyl compounds to interact with multiple sites of Lewis acidity when they are oriented appropriately within a single multidentate reagent. Spectroscopic changes associated with multiple coordination indicate that the C═O bond is weakened, so multidentate Lewis acids may prove to be particularly effective agents for the recognition, binding, and chemical activation of carbonyl compounds.

Experimental Section

Ether and tetrahydrofuran were dried by distillation from the sodium ketyl of benzophenone, hexane was dried by distillation from CaH_2, and *N*,*N*-diethylformamide was purified by distillation under reduced pressure and then dried over 4 Å molecular sieves. Trifluoromethanesulfonic acid was dried over P_2O_5 and distilled, and $AgOSO_2CF_3$ was dehydrated before use by heating it at 130 °C/0.2 Torr for 12 h. All other reagents were commercial products that were used without further purification.

2:1 Complex of *N*,*N*-Diethylformamide with the Bis(trifluoromethanesulfonate) Salt of Cyclic *μ*-Hydroxide 7. A suspension of oxo[*μ*-(3,4,5,6-tetramethyl-1,2-phenylene)]dimercury (**6**; 75 mg, 0.14 mmol)[6] in ether (3 mL) was stirred at 25 °C under dry N_2 and treated with trifluoromethanesulfonic acid (15 *μ*L, 0.16 mmol), and the mixture was kept at 25 °C for 12 h. Solids were then separated by centrifugation, washed with ether, dried in vacuo at 25 °C, and dissolved in the minimum amount of *N*,*N*-diethylformamide at 110 °C. The solution was cooled and mixed with hexane, and then the lower phase was separated and allowed to crystallize. This yielded colorless crystals of the 2:1 complex of *N*,*N*-diethylformamide with the bis(trifluoromethanesulfonate) salt of cyclic *μ*-hydroxide **7** (60 mg, 0.037 mmol, 53%): IR (Nujol) 1648 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 1.00 (t, 6H, $^3J = 7.1$ Hz), 1.08 (t, 6H, $^3J = 7.1$ Hz), 2.19 (s, 12H), 2.41 (s, 12H), 3.22 (q, 4H, $^3J = 7.1$ Hz), 3.25 (q, 4H, $^3J = 7.1$ Hz), 5.67 (s, 2H), 7.98 (s, 2H); ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 12.7, 14.8, 17.1, 26.5, 35.7, 40.9, 120.7 (q, $^1J_{C-F} = 322$ Hz), 135.3, 138.4, 156.7, 162.0; ^{199}Hg NMR (71.6 MHz, DMSO-d_6) δ −1423. Anal. Calcd for $C_{32}H_{48}F_6Hg_4N_2O_{12}S_2$: C, 24.00; H, 3.02. Found: C, 23.84; H, 3.05.

Dichloro(3,4,5,6-tetramethyl-1,2-phenylene)dimercury (9). At 25 °C under dry N_2, dry gaseous HCl (30 mL, 1.3 mmol) was added slowly by syringe to a stirred suspension of *μ*-(3,4,5,6-tetramethyl-1,2-phenylene)bis(trifluoroacetato-*O*)dimercury (**3**; 500 mg, 0.66 mmol)[6] in tetrahydrofuran (10 mL). The mixture was kept at 25 °C for 1 h, volatiles were removed by evaporation under reduced pressure, and the residual solid was washed with CH_2Cl_2. The washed solid was then treated with tetrahydrofuran, and the mixture was filtered. Removal of solvent from the filtrate by evaporation under reduced pressure left a residue of analytically pure dichloro(3,4,5,6-tetramethyl-1,2-phenylene)dimercury (**9**), which was isolated in the form of a colorless solid (290 mg, 0.48 mmol, 73%): mp 140 °C (dec); IR (KBr) 2933, 1432, 1385, 1195 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 2.14 (s, 6H), 2.32 (s, 6H); ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 17.1, 26.5, 134.4, 137.6, 160.7. Anal. Calcd for $C_{10}H_{12}Cl_2Hg_2$: C, 19.88; H, 2.00. Found: C, 19.98; H, 2.12.

2:1 Complex of *N*,*N*-Diethylformamide with *μ*-(3,4,5,6-Tetramethyl-1,2-phenylene)bis(trifluoromethanesulfonato-*O*)dimercury (8). A mixture of dichloro(3,4,5,6-tetramethyl-1,2-phenylene)dimercury (**9**; 39 mg, 0.065 mmol) and $AgOSO_2CF_3$ (38 mg, 0.15 mmol) in ether (8 mL) was stirred in the dark at 25 °C under dry Ar. After 45 min, the resulting suspension was treated with *N*,*N*-diethylformamide (0.30 mL, 2.7 mmol). After 12 h, the mixture was centrifuged, and the supernatant solution was separated and concentrated by partial evaporation under reduced pressure. The concentrate was mixed with hexane, and the supernatant phase was removed. Crystallization of the lower phase yielded colorless moisture-sensitive needles of the 2:1 complex of *N*,*N*-diethylformamide with *μ*-(3,4,5,6-tetramethyl-1,2-phenylene)bis(trifluoromethanesulfonato-*O*)dimercury (**8**; 58 mg, 0.056 mmol, 86%): IR (Nujol) 1643 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 1.00 (t, 6H, $^3J = 7.1$ Hz), 1.08 (t, 6H, $^3J = 7.1$ Hz), 2.17 (s, 6H), 2.38 (s, 6H), 3.22 (q, 4H, $^3J = 7.1$ Hz), 3.25 (q, 4H, $^3J = 7.1$ Hz), 7.98 (s, 2H); ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 12.7, 14.8, 17.1, 26.6, 35.7, 40.9, 120.7 (q, $^1J_{C-F} = 322$ Hz), 135.0, 137.8, 155.1, 162.0.

X-ray Crystallographic Studies of the 2:1 Complex of *N*,*N*-Diethylformamide with the Bis(trifluoromethanesulfonate) Salt of Cyclic *μ*-Hydroxide 7 and the 2:1 Complex of *N*,*N*-Diethylformamide with *μ*-(3,4,5,6-Tetramethyl-1,2-phenylene)bis(trifluoromethanesulfonato-*O*)dimercury (8). Data were collected on an Enraf-Nonius CAD-4 diffractometer. Cell constants were obtained using 25 well-centered reflections ($40° \leq 2\theta \leq 45°$). Five standard reflections were measured every 1 h of exposure time and showed only small fluctuations. The data were corrected for absorption by Gaussian integration. The structure was solved by direct methods using SHELXS-86.[20] Full-matrix least-squares refinement on F^2 was carried out with SHELX-76.[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined isotropically.

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Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters, and distances to weighted least-squares planes for the 2:1 complex of diethylformamide with the bis(trifluoromethanesulfonate) salt of *μ*-hydroxide **7** and the 2:1 complex of diethylformamide with bis(trifluoromethanesulfonate) **8** (32 pages). Ordering information is given on any current masthead page.

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