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Host−Guest Chemistry of 1,2-Bis(chloromercurio)tetrafluorobenzene. Chelation of the Carbonyl Oxygen Atom of Acetone by a Bidentate Lewis Acid

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Incremental addition of DMF or DMSO to a solution of 1,2-bis(chloromercurio)tetrafluorobenzene (**3**) in acetone results in a change of the ^{199}Hg NMR chemical shift of **3**. The titration curves thus obtained can be fitted and indicate the formation of the 1:1 host−guest complexes **3**·μ_2-DMF (**4**) and **3**·μ_2-DMSO (**5**). The stability constants of **4** and **5** have been determined and are respectively equal to 1.8 (±0.2) M^{-1} and 8.0 (±0.8) M^{-1}. The X-ray crystal structures of **4** and **3**·μ_2-acetone (**6**) have been determined. In the structure of **4**, the carbonyl oxygen atom is coordinated to three mercury atoms and has a distorted-tetrahedral geometry. In **6** however, the acetone oxygen is coordinated to only two mercury atoms and exhibits a trigonal-planar geometry. While it is difficult to detect any metrical changes undergone by the organic substrates upon chelation, the IR carbonyl stretching frequency of **4** (ν_{CO} 1635 cm^{-1}) and **6** (ν_{CO} 1639 cm^{-1}) indicates that the carbon oxygen bond is weakened. Accordingly, the ^{13}C CP/MAS NMR carbonyl carbon chemical shifts of **4** (167 ppm) and **6** (215 ppm) provide evidence for a substantial polarization of the carbonyl. By comparison of the ^{13}C CP/MAS NMR carbonyl carbon chemical shift, the Lewis acidity of **3** toward acetone can be evaluated to be just inferior to that of $MgCl_2$. Finally, both **4** and **6** have complex and highly networked supramolecular structures which result from intermolecular Hg···Cl and Hg···F or Hg···O contacts.

Introduction

The study of neutral polyfunctional Lewis acids shows that these compounds can serve as polydentate hosts for nucleophilic substrates.[1] Although this research has focused in its largest part on the binding of anions,[1a,c−e,2−6] recent reports clearly demonstrate that these compounds are valuable Lewis acid catalysts for organic reactions involving carbonyl compounds such as aldehydes and ketones.[7] The high catalytic activity observed in these reactions results presumably from the ability of the bifunctional Lewis acid to chelate the carbonyl oxygen atom.

Given the propensity of polyfunctional organomercurials to form crystalline chelate complexes with solvent molecules such as sulfoxides and amides,[8] simple bifunctional Lewis acids such 1,2-bis(chloromercurio)benzene (**1**)[9] and 1,8-bis(chloromercurio)naphthalene (**2**)[10] have been used to study the chelation of neutral

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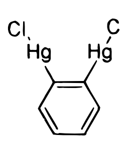
substrates containing basic terminal oxo functions.



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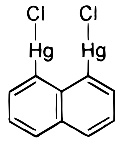

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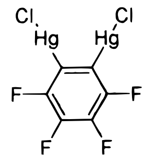

3

Thus, in a series of elegant studies,[9,11] Wuest et al. have shown that compounds containing the 1,2-bis(mercury)-benzene motifs crystallize from formamide solvents to yield complexes in which the carbonyl oxygen atom is coordinated to two and sometimes four mercury centers.[12] In contrast, however, the preparation of bimolecular complexes in which two Lewis acids interact concomitantly with the carbonyl oxygen of a weakly basic carbonyl compound such as a ketone has yet to be completed.

The use of electron-withdrawing backbones in polydentate organomercurials constitutes an efficient method for increasing the acceptor properties of the mercury centers. This principle is well illustrated by the work of Hawthorne et al. on mercuracarborands as ligand for anions.[3] Also, as demonstrated by Shur et al., perfluorinated *o*-phenylenemercury forms isolable adducts with a variety of anions while *o*-phenylenemercury shows only poor acceptor properties.[4] Taking these observations into account, it occurred to us that the use of a perfluorinated bidentate Lewis acid might be of special interest for the chelation of weakly basic organic substrates such as ketones. Our work was further motivated by the ongoing studies of simple ketones in superacid solutions[13] and in Brønsted acid zeolites[14] as well as in mononuclear Lewis acid adducts.[15,16]

In this contribution, we report our findings on the host−guest chemistry of 1,2-bis(chloromercurio)tetrafluorobenzene (**3**)[17] vis-à-vis a series of neutral organic substrates which have led us to isolate the first chelate complex between a ketone and a bifunctional Lewis acid.[18]

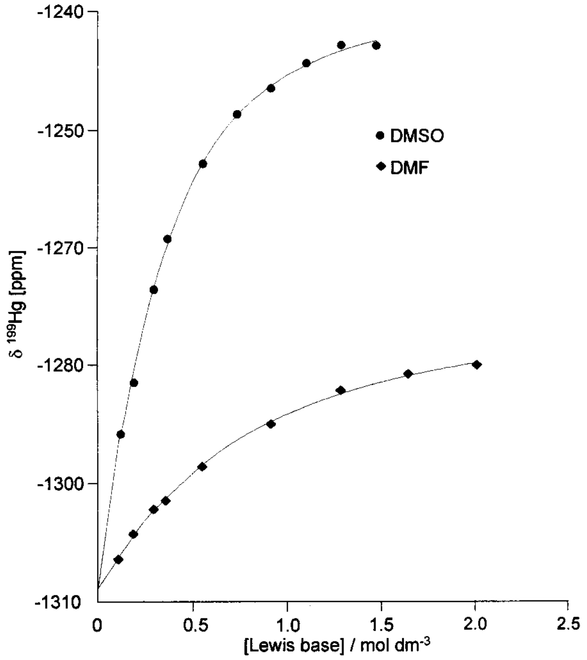

Figure 1. ^{199}Hg chemical shift of **3** in acetone vs concentration of added DMF or DMSO. [**3**] = 0.37 mol dm^{-3}.

Results and Discussion

Host−Guest Solution Studies. Compound **3** was prepared according to the published procedure[17] and was characterized by ^{19}F and ^{199}Hg NMR spectroscopy. The ^{19}F NMR spectrum of **3** exhibits two signals whose multiplicity is in agreement with the existence of a higher order AA′BB′ spin system. Because of ^{199}Hg−^{19}F nuclear spin-coupling interactions each ^{19}F NMR signal exhibits a pair of low-intensity satellites and the ^{199}Hg NMR signal is split into a complex multiplet. Compound **3** dissolves only in polar solvents such as acetone, DMF, and DMSO. According to the Gutmann scale, acetone exhibits significantly lower donor ability than do DMF and DMSO.[19] The former solvent was therefore selected as the medium for solution host−guest coordination studies. Upon incremental addition of DMSO and DMF to a solution of **3** in acetone, the ^{199}Hg NMR resonance undergoes a drastic downfield shift (Figure 1). While a change of the solvent polarity can be held responsible for this phenomenon, it is interesting to note that, in both cases, the curves rapidly reach a plateau. This behavior is characteristic of the almost quantitative formation of host−guest complexes. Since the stoichiometry of the host−guest complexes in solution remained quite elusive, the curves were tentatively fitted on the basis of two hypothetical models.[20] The possible formation of 1:2 host−guest complexes was

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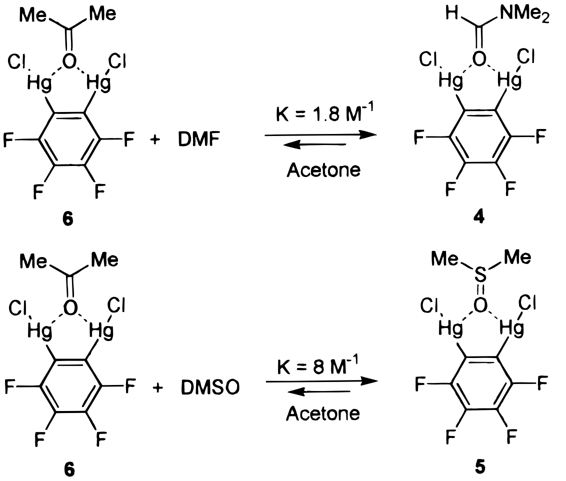
Scheme 1



first considered. In both cases, however, the refinements were unstable and unreliable stability constants were obtained. In contrast, when the curves were fitted on the basis of the formation of a 1:1 complex, stable refinements were obtained and stability constants of 1.8 (±0.2) and 8.0 (±0.8) M^{-1} could be determined for **3**·μ_2-DMF (**4**) and **3**·μ_2-DMSO (**5**), respectively (Scheme 1). Although the magnitude of these stability constants appears relatively small, it must be kept in mind that the titration experiments are performed in acetone and that the latter solvent might therefore have a leveling effect. In fact, when compound **3** is crystallized from acetone, **3**·μ_2-acetone (**6**) is isolated (vide infra), thus suggesting that solutions of **3** in acetone contain **6** as a major species. Thus, despite its low Gutmann number[19] and associated low basicity, acetone is a noninnocent solvent which competes with the guest species.

Solid-State Studies. With the study of carbonyl chelation as a goal, special efforts were made to obtain crystalline complexes in which **3** is associated with a carbonyl-containing guest molecule such as DMF or acetone. Fortunately, slow evaporation of the solvent from a DMF and an acetone solution of **3** resulted in the crystallization of the chelate host−guest complexes **3**·μ_2-DMF (**4**) and **3**·μ_2-acetone (**6**), respectively. It is noteworthy that the isolation of the 1:1 complexes **4** and **6** corroborates the results of the acetone solution studies. While compound **4** is stable for several weeks at room temperature, compound **6** decomposes rapidly under a dry atmosphere through loss of its acetone component to afford pure **3**.

Owing to the negative character of the oxygen atom in DMF, this substrate exhibits high donor ability and has often been considered as a guest for bidentate organomercurials.[11,12] In contrast, however, the chelation of ketones by bidentate Lewis acids remains a rare phenomenon which has been postulated on a few occasions,[7,21] and is limited to the sole example of a dialuminum complex which features an intramolecular version of this linkage.[22] Compound **6** is thus the first bimolecular ketone chelate complex. Its isolation substantiates the enhanced Lewis acidity of **3**. Note that

Table 1. Crystal Data, Data Collection, and Structure Refinement for 4 and 6

	4	**6**
	Crystal Data	
formula	$C_9H_7Cl_2F_4Hg_2NO$	$C_9H_6Cl_2F_4Hg_2O$
M_r	693.24	678.22
cryst syst	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
a (Å)	19.901(1)	6.654(1)
b (Å)	10.923(1)	10.269(2)
c (Å)	13.734(1)	21.238(3)
α (deg)	90	93.57(1)
β (deg)	106.71(1)	99.00(1)
γ (deg)	90	108.89(1)
V (Å^3)	2859.4(4)	1346.2(4)
ρ_{calcd} (g cm^{-3})	3.221	3.346
Z	8	4
F(000) (e)	2448	1192
μ(Mo Kα) (cm^{-1})	218.6	232.1
	Data Collection	
T (°C)	−79	−70
scan mode	ω	ω/θ
hkl range	−25 to +21, 0−13, −17 to +17	−8 to +8, −13 to +13, 0−27
$[(\sin\theta)/\lambda]_{max}$ (Å^{-1})	0.64	0.64
no. of measd rflns	6103	5840
no. of unique rflns [R_{int}]	3120 [0.0319]	5833 [0.2369]
no. of rflns used for refinement	2962	5788
abs cor	DIFABS	ψ scans
T_{min}/T_{max}		0.23/0.99
	Refinement	
no. of refined params	172	325
final R values ($I > 2\sigma(I)$)		
R1[a] (%)	0.0236	0.0511
wR2[b] (%)	0.0539	0.1321
ρ_{fin}(max/min) (e Å^{-3})	1.549/−1.582, at Hg atoms	2.718/−3.975, at Hg atoms

[a] $R1 = \sum(F_o - F_c)/\sum F_o$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$: $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0306$ (**4**), 0.0659 (**6**); $b = 1.21$ (**4**), 23.97 (**6**).

bridging acetone molecules have been observed in the structure of inorganic alkali-metal salts.[23]

Solid-State Characterization of 3·μ_2-DMF (4). Compound **4** crystallizes in the monoclinic space group $C2/c$ with eight molecules in the unit cell (Table 1). The carbonyl oxygen atom is coordinated to both mercury centers Hg(1) and Hg(2) (Figure 2). The resulting Hg(1)−O and Hg(2)−O bonds are approximately perpendicular to the C(1)−Hg(1)−Cl(1) and C(2)−Hg(2)−Cl(2) sequences, respectively. The Hg(1)−O (2.653(4) Å) and Hg(2)−O (2.746(4) Å) bonds are shorter than the sum of the van der Waals radii of oxygen (1.54 Å)[24] and mercury (1.73−2.00 Å).[25] They are also slightly shorter than those measured in **1**·μ_2-DMF (2.681(13) and 2.777(13) Å),[9] which indicates that **3** is a stronger Lewis acid than **1**. Examination of the coordination environment at oxygen indicates the presence of an additional linkage with the mercury atom of a neighboring complex.

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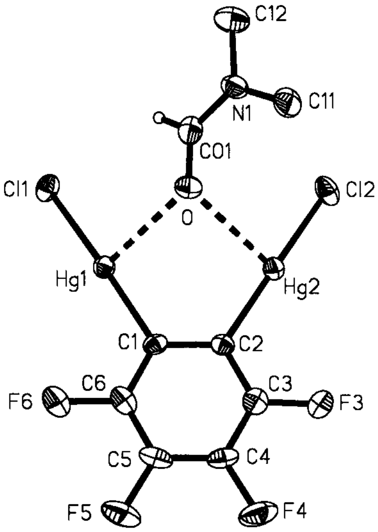

Figure 2. Structure of **4** in the crystal (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Hg(1)−O = 2.653(4), Hg(2)−O = 2.746(4), Hg(1)−C(1) = 2.047(6), Hg(2)−C(2) = 2.043(5), Hg(1)−Cl(1) = 2.317(1), Hg(2)−Cl(2) = 2.308(1), C(01)−O = 1.239(8); C(01)−O−Hg(1) = 122.0(4), C(01)−O−Hg(2) = 118.0(4), Hg(1)−O−Hg(2) = 84.0(1), C(1)−Hg(1)−Cl(1) = 175.9(2), C(2)−Hg(2)−Cl(2) = 176.5(2), C(1)−Hg(1)−O = 90.4(2), C(2)−Hg(2)−O = 88.6(2), O−Hg(1)−Cl(1) = 93.0(1), O−Hg(2)−Cl(2) = 93.8(1).

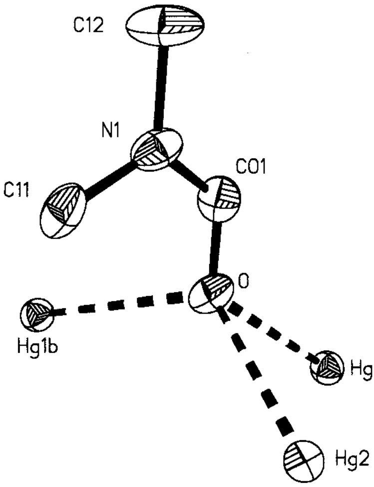

Figure 3. View showing the distorted-tetrahedral coordination of the DMF oxygen atom in **4**. Selected bond angles (deg): C(01a)−O−Hg(1a) = 122.0(4), C(01a)−O−Hg(2a) = 118.0(4), C(01a)−O−Hg(1b) = 109.7.0(4), Hg(1a)−O−Hg(2a) = 84.0(1), Hg(1a)−O−Hg(1b) = 90.8(1), Hg(1b)−O−Hg(2a) = 126.5(1).

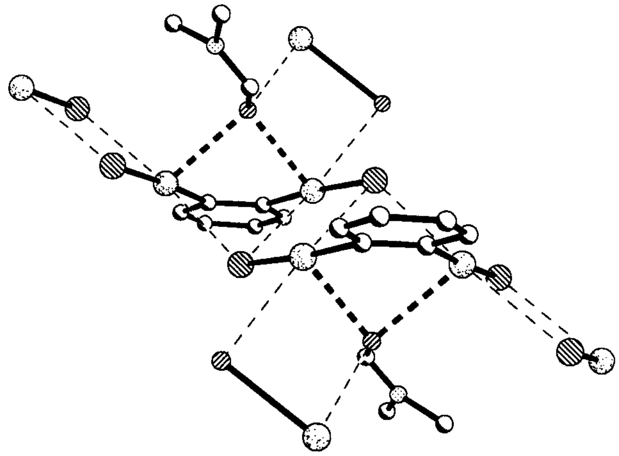

Figure 4. View of a dimeric unit in the structure of **4**. The contacts with atoms belonging to neighboring molecules are also depicted. The fluorine atoms have been omitted for clarity.

Table 2. Intermolecular Hg···Cl and Hg···F Distances (Å) in the Supramolecular Structure of 4

Hg(1)−Cl(1)^a = 3.223
Hg(2)−Cl(1)^a = 3.244
Hg(1)−O(1)^b = 3.046
Hg(2)−Cl(2)^c = 3.159

^{a} $-x, -y, -z$. ^{b} $-x, -y, -z + 1/2$. ^{c} $-x - 1/2, y + 1/2, -z$.

Although this intermolecular Hg(1b)−O distance (3.046(4) Å) is longer than Hg(1)−O and Hg(2)−O, it remains smaller than the sum of the van der Waals radii[24,25] and indicates the presence of a weak interaction. The resulting coordination geometry of the oxygen atom approaches that of a distorted tetrahedron (Figure 3). The standard deviations of the C−O and C−N bond distances are too large to confirm any changes in the electronic structure of DMF. However, a consequential weakening of the C−O bond is readily detected by infrared spectroscopy. In comparison to neat DMF (ν_{CO} 1675 cm^{-1}), the stretching frequency of the carbonyl group in **4** (ν_{CO} 1635 cm^{-1}) is shifted by 40 cm^{-1} to lower wavenumbers. The C−O stretching frequency of **4** is much weaker than that detected for **1**·μ_2-DMF (ν_{CO} 1655 cm^{-1}), which further substantiates the stronger Lewis acidity of **3** with respect to **1.** The weakening observed in **4** is in fact of magnitude similar to that observed upon coordination of diethylformamide by a cationic tetranuclear mercury host.[11b] In the ^{13}C CP/MAS NMR spectrum, the resonance of the carbonyl carbon of **4** (δ 167 ppm) is shifted to lower frequency by 5 ppm with respect to neat DMF. This coordination shift is much weaker than that detected for the carbonyl carbon of **6** (vide infra), which can be rationalized by invoking π-electron donation from the nitrogen atom of DMF to the carbonyl carbon atom in **4**.

In the crystal, intermolecular sub-van der Waals Hg···Cl contacts ranging from 3.159 to 3.244 Å (r_{vdw}(Cl) = 1.58−1.78 Å,[24] r_{vdw}(Hg) = 1.73−2.00 Å)[25] are responsible for the association of molecules of **4** into dimeric units (Figure 4, Table 2). These dimeric units are formed by reciprocal chelation of a Hg−Cl moiety of one molecule by its bidentate counterpart, a phenomenon also observed in the structures of {[2,4,6-$(CH_3)_3$-C_6H_2]N[$(CH_2)_2$HgCl]$_2$}[26] and *meso*-1,3-[C_6H_4(CHSi-Me_3HgCl)$_2$].[27] Each dimer interacts with two neighbors by formation of head-to-tail Hg_2Cl_2 bridges and two other neighbors by formation of Hg_2O_2 bridges (Figure 4, Table 2) to from a highly cross-linked three-dimensional network.[2b]

Solid-State Characterization of 3·μ_2-Acetone (6). Compound **6** crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules (I and II) in the asymmetric unit (Table 1). The metrical parameters for molecules I and II are very similar. In each molecule, the oxygen atom of the chelated acetone molecule is

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(26) Deacon, G. B.; Gatehouse, B. M.; Guddat, L. W.; Ney, S. C. *J. Organomet. Chem.* **1989**, *375*, C1.

(27) Tschinkl, M.; Schier, A.; Riede, J.; Mehltretter, G.; Gabbaï, F. P. *Organometallics* **1998**, *17*, 2921−2923.

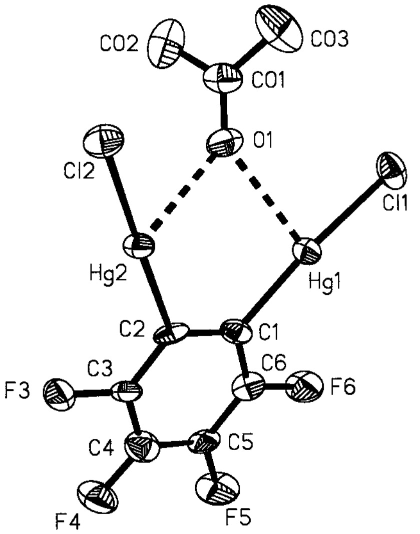

Figure 5. Structure of **6** in the crystal (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths (Å) and angles (deg) [value for the second independent molecule in brackets]: Hg(1)−O(1) = 2.679(13) [2.800(13)], Hg(2)−O(1) = 2.776(14) [2.693(13)], Hg(1)−C(1) = 2.04(1) [2.04(2)], Hg(2)−C(2) = 2.07(1) [2.07(1)], Hg(1)−Cl(1) = 2.307(4) [2.311(4)], Hg(2)−Cl(2) = 2.303(4) [2.307(4)], C(01)−O(1) = 1.21(2) [1.17(2)]; C(01)−O(1)−Hg(1) = 140.7(12) [141.8(12)], C(01)−O(1)−Hg(2) = 133.5(12) [133.0(12)], Hg(1)−O(1)−Hg(2) = 85.3(4) [84.5(4)], C(1)−Hg(1)−Cl(1) = 173.0(5) [173.4(4)], C(2)−Hg(2)−Cl(2) = 177.7(4) [177.8(4)], C(1)−Hg(1)−O(1) = 99.7(5) [99.5(5)], C(2)−Hg(2)−O(1) = 98.6(5) [98.4(5)], O(1)−Hg(1)−Cl(1) = 86.7(3) [86.2(3)], O(1)−Hg(2)−Cl(2) = 81.6(3) [81.3(3)].

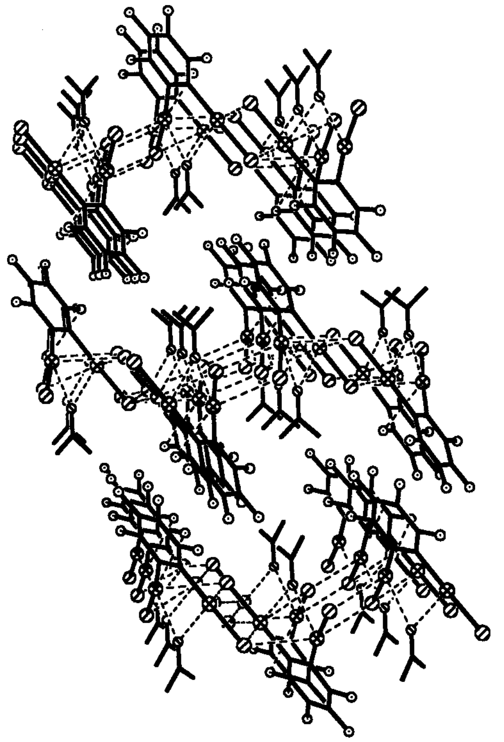

Figure 6. View showing the layered structure of **6**.

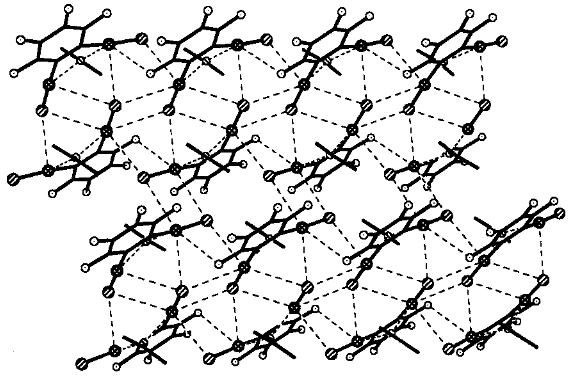

Figure 7. View of layer of type A in the crystal of **6**. The formation of highly networked two-dimensional sheets is evident from this view.

positioned in such a manner that the resulting Hg−O bonds are approximately perpendicular to the C−Hg−Cl sequences (Figure 5). The Hg−O bonds of 2.679(13) and 2.776(14) Å are shorter than the sum of the van der Waals radii of oxygen[24] and mercury[25] and can be compared with the average distance of 2.712 Å obtained in the structure of a troponoid dithio-crown ether bis(mercury dichloride) complex which contains a carbonyl function doubly coordinated to two mercury dichloride moieties.[28] The coordination geometry of the oxygen atoms is trigonal-planar (sum of bond angles 359.5° (in I) and 359.3° (in II)). This feature contrasts with the structure of **4**, where the oxygen atom exhibits a strong pyramidality. Although it is tempting to suggest that each lone pair of the carbonyl oxygen atom interacts with an empty p-orbital of the mercury centers, it must be indicated that the dihedral angle of 68.6° between the C(02)−C(01)−C(03) and Hg(1)−O(1)−Hg(2) planes is large (67.7° for the corresponding angle in II) while the Hg(1)−O(1)−Hg(2) angle of 85.3° is small (84.5° for the corresponding angle in II). While the accuracy of the measurement did not permit us to determine if the chelation of the acetone results in a lengthening of the C=O bond, the carbonyl IR stretching frequency in **6** (ν_{CO} 1693 cm^{-1}) is 23 cm^{-1} weaker than that of neat liquid acetone (ν_{CO} 1716 cm^{-1}). Further insights on the chemical consequences of the chelation were gained by measuring a ^{13}C CP/MAS NMR spectrum. This measurement indicates that the carbonyl carbon resonance (δ 215 ppm) of **6** is shifted to lower frequency by 10 ppm when compared to that of neat acetone. For comparison, in superacidic solutions, the carbonyl carbon of acetone exhibits a very deshielded chemical shift of 250 ppm.[13] Analogously, a shift of 245 ppm is observed when acetone is coordinated to Al_2Cl_6.[15a] The chemical shift observed in **6** is in fact in the same range as that of acetone adsorbed on $MgCl_2$ (δ 221 ppm) or on acid zeolite such as HZSM-5 (δ 223 ppm).[14a]

In the crystal, compound **6** adopts a layered structure. There are two types of layers (A and B) which alternate along the *z* axis (Figure 6). Although layers A and B have very similar 2-D topologies, the A layer contains only molecules of type I, while the B layer contains only molecules of type II. In each layer, the formation of dimeric units can first be recognized (Figure 7). As in **4**, these dimers are formed by reciprocal chelation of a Hg−Cl moiety of one molecule by its bidentate counterpart.[26,27] Additional van der Waals Hg···Cl and Hg···F contacts (r_{vdw}(F) = 1.30−1.38 Å,[24] r_{vdw}(Cl) = 1.58−1.78 Å,[24] r_{vdw}(Hg) = 1.73−2.00 Å)[25] (Table 3)

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[28] Mori, A.; Kubo, K.; Kato, N.; Takeshita, H.; Shiono, M.; Achiwa, N. *Heterocycles* **1998**, *47*, 149−152.

Table 3. Intermolecular Hg···Cl and Hg···F Distances (Å) in the Supramolecular Structure of 6

Hg(1)−Cl(1)^a = 3.327
Hg(1)−Cl(2)^b = 3.207
Hg(1)−F(3)^c = 3.301
Hg(2)−Cl(1)^d = 3.225
Hg(2)−Cl(2)^b = 3.523
Hg(2)−Cl(2)^e = 3.540
Hg(3)−Cl(3)^f = 3.529
Hg(3)−Cl(3)^g = 3.534
Hg(3)−Cl(4)^d = 3.225
Hg(4)−Cl(3)^f = 3.208
Hg(4)−Cl(4)^h = 3.329
Hg(4)−F(12)^c = 3.305

[a] $-x + 1, -y + 1, -z + 1$. [b] $-x + 2, -y + 2, -z + 1$. [c] $x - 1, y, z$. [d] $x + 1, y, z$. [e] $-x + 3; -y + 2; -z + 1$. [f] $-x, -y + 1, -z$. [g] $-x + 1, -y + 1, -z$. [h] $-x, -y + 2, -z$.

connect the dimers leading to the highly networked structure depicted in Figure 7.

Conclusion

Our solution studies indicate that compound **3** forms 1:1 host−guest complexes with basic substrates containing terminal oxo groups. These studies also indicate that **3** exhibits a moderate selectivity (DMSO > DMF > acetone) which follows the Gutmann donor number order DMSO (DN = 29.8) > DMF (DN = 24) > acetone (DN = 17).[19] The isolation of the crystalline 1:1 host−guest complexes **4** and **6** corroborates the results obtained on the stoichiometry of the host−guest complexes in solution. The geometry observed at the carbonyl oxygen atom in both **4** and **6** is hard to rationalize on the basis of classical frontier-orbital arguments and suggests that dipole−dipole interactions between the carbonyl substrate and **3** contribute to the stability of the host−guest complexes. While it is difficult to detect any metrical changes undergone by the organic substrates upon chelation, both the IR and ^{13}C CP/MAS NMR spectra of **4** and **6** indicate that a substantial polarization of the carbonyl occurs. By comparison of the carbonyl carbon ^{13}C CP/MAS NMR chemical shift, the Lewis acidity of **3** toward acetone can be evaluated to be just lower than that of $MgCl_2$. Finally, it should be emphasized that the preparation and structural characterization of a bimolecular ketone chelate complex such as **6** constitute a first in the chemistry of bifunctional Lewis acids and show that the use of a bidentate system with enhanced acidity renders the complexation of weak donors possible.

Experimental Section

General Considerations. Nuclear magnetic resonance spectra in solution were obtained on a JEOL-GX 400 instrument (400 MHz for ^{1}H, 100.5 MHz for ^{13}C, 71.56 MHz for ^{199}Hg) and on a JEOL-JNM-LA 400 instrument (400 MHz for ^{1}H, 376.5 MHz for ^{19}F). Neat $HgMe_2$ was used as an external standard for the solution ^{199}Hg NMR spectra. The proton and carbon signals of the deuterated solvent were used as internal standard for the ^{1}H and ^{13}C NMR spectra, respectively. ^{19}F NMR chemical shifts are reported relative to CF_3COOH. The solid-state ^{13}C CP/MAS NMR spectra were recorded on a Bruker MSL 300 spectrometer operating at a field strength of 7.05 T. Cross-polarization and high-power proton decoupling were applied with a 90° pulse time of 5 μs, a contact time of 5 ms, and a recycle delay of 8 s. ^{13}C NMR shifts are referenced to an external sample of adamantane, with the signal at low frequency being set to 29.472 ppm relative to TMS. Approximately 50 mg of the sample was packed into 4 mm ZrO_2 Bruker rotors with Kel-F caps. The rotor spinning speeds were 8 and 7 kHz for **6** and **4**, respectively. All NMR measurements were carried out at 25 °C. The Laboratory for Microanalysis at Technische Universität München performed the elemental analyses. The infrared spectra were recorded in KBr pellets. All melting points were measured on samples in sealed capillaries and are uncorrected. All solvents were distilled prior to use and stored over molecular sieves. All commercially available starting materials were purchased from Aldrich Chemicals and used as provided.

Characterization of 1,2-Bis(chloromercurio)tetrafluorobenzene. Compound **3** was synthesized according to the literature procedure.[17] ^{19}F NMR (acetone-d_6): δ −37.80 (m$_c$, $^3J_{F,F}$ = 24.0 Hz, $^4J_{F,F}$ = 6.0 Hz, $J_{F,Hg}$ = 620 Hz, 2 F, F-3/6), −77.67 (m$_c$, $^3J_{F,F}$ = 24.0 Hz, $^4J_{F,F}$ = 6.0 Hz, $J_{F,Hg}$ = 233 Hz, 2 F, F-3/6). ^{13}C{^{1}H} NMR (acetone-d_6): δ 139.8 (m$_c$, $^1J_{C,F}$ = 260 Hz, C-3/6), 142.0 (br, C-1/2), 149.4 (m$_c$, $^1J_{C,F}$ = 234 Hz, C-4/5). ^{199}Hg NMR (acetone-d_6): −1309 (m).

Synthesis of 1,2-Bis(chloromercurio)tetrafluorobenzene−Dimethylformamide Adduct (4). A DMF (2 mL) solution containing 62 mg of **3** was placed in a vial and allowed to stand at room temperature in a well aerated fume hood. Over a period of 5 days, all solvents slowly evaporated to give a quantitative yield of crystalline **4** (69 mg). Compound **4** is stable for weeks under ambient conditions. Mp: 208−210 °C. Anal. Calcd for $C_9H_7F_4Cl_2Hg_2NO$: C, 15.58; H, 1.01; N, 2.02. Found: C, 15.63; H, 1.06; N, 2.06. CP/MAS NMR data: ^{1}H, δ 3.4 (br, CH_3), 8.2 (OCH); ^{13}C, δ 34.0, 36.7 (CH_3), 140.0−147.2 (C-3/6, C-1/2, C-4/5), 166.8 (CO). IR: 3447, 2967, 2926, 1655, 1635, 1480, 1426, 1418, 1376, 1314, 1289, 1254, 1109, 1088, 1011, 822, 772, 665 cm^{-1}.

Synthesis of 1,2-Bis(chloromercurio)tetrafluorobenzene−Acetone Adduct (6). An acetone (2 mL) solution containing 62 mg of **3** was placed in a vial and allowed to stand at room temperature in a well aerated fume hood. The aperture of the vial was partially closed. All solvents slowly evaporated over a period of 4 h to give a quantitative yield of crystalline **6** (67 mg). Compound **6** rapidly decomposes at room temperature by loss of acetone to afford pure **3,** which precluded the collection of satisfactory elemental analysis data. CP/MAS NMR: ^{1}H, δ 2.1 (CH_3); ^{13}C, δ 31.65 (CH_3), 140.8−147.4 (C-3/6, C-1/2, C-4/5), 215.5 (CO). IR: 3447, 1693, 1483, 1420, 1356, 1316, 1292, 1231, 1090, 1005, 822, 770 cm^{-1}.

^{199}Hg NMR Titration Experiment. The titration curves depicted in Figure 1 were obtained by incremental addition of small amounts of the titrant (DMF or DMSO) to an acetone-d_6 solution (0.6 mL) of **3** (134.7 mg, 0.22 mmol). A 25 μL syringe was used to add the titrant directly into the NMR tube containing the solution of **3**. After each addition the ^{199}Hg NMR chemical shift of the sample was measured. The program EQNMR was used to calculate the stability constant K. The data were not corrected for the slight change in volume produced by the addition of titrant. K is defined as K = [**3**·DMF]/{[**3**][DMF]}. The approximation that [**3**] = [**3**·acetone] can be made by considering that "free" **3** in acetone exists as **3**·acetone. The concentration of acetone is considered to be constant and has therefore not been taken into account in the expression of K.

Crystal Structure Determinations. Specimens of suitable quality and size of compounds **4** and **6** were mounted in glass capillaries. For **6**, to avoid decomposition, the crystal was rapidly transferred from a saturated acetone atmosphere into a capillary and into the cooled nitrogen stream of the low-temperature device. An Enraf-Nonius CAD4 diffractometer (Mo Kα radiation, (Mo Kα) = 0.710 73 Å) was used for measurements of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for either compound. Lp correction was applied, and intensity data were corrected for absorption effects. The structures were solved by direct methods (SHELXS-86) and completed by full-matrix least-squares techniques against F^2 (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{\mathrm{iso}}(\mathrm{fix}) = 1.5U_{\mathrm{eq}}$ of the attached C atom). Further information on crystal data, data collection, structure refinement, and metrical parameters are summarized in Tables 1−3 as well as in the corresponding figure captions.

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Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, all bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates and thermal parameters for **4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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