Notes

Selective Binding of the Keto Form of Acetylacetone by Cyclic Trimeric Perfluoro-*o*-phenylenemercury. Quantitative Shift of the Keto−Enol Equilibrium in Acetylacetone Toward Its Keto Form Stabilized by the Complexation

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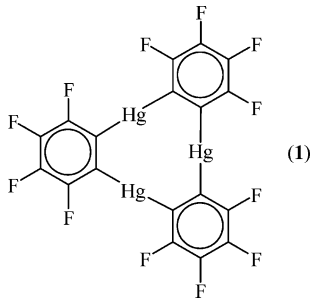
*Summary: This paper reports on the remarkable ability of cyclic trimeric perfluoro-o-phenylenemercury (o-$C_6F_4Hg)_3$ (**1**) to bind selectively the less stable keto form of acetylacetone (AA) with the formation of a sandwich complex {[(o-$C_6F_4Hg)_3$]$_2$(AA)} (**2**), wherein the molecule of AA is disposed between the mutually parallel planes of two macrocycles and is bonded to each of them via the cooperative coordination of its carbonyl oxygen atoms by all three Hg centers of the neighboring molecule of **1**. The synthesized **2** is the first example of a structurally characterized complex containing the keto form of AA as a ligand.*

Introduction

Keto−enol equilibria play an important role in organic chemistry, determining the chemical behavior of tautomeric systems. Therefore, searches for approaches that would allow the quantitative shift of such equilibria toward one or another tautomeric form are of great interest. One of the ways for solving this intriguing problem is the use of specific supramolecular host−guest interactions for the selective binding of the corresponding keto or enol form. Among potential hosts that could be suitable for this purpose, macrocyclic multidentate Lewis acids, named anticrowns,[1] seem to be very promising.[2]

In our continuing studies aimed at development of supramolecular and catalytic chemistry of anticrowns, we have previously demonstrated the remarkable property of cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-$C_6F_4Hg)_3$ (**1**)[3] to bind efficiently various anionic species with the formation of host−guest complexes of the unique structures.[2a,c] It has also been shown that this macrocycle readily coordinates different neutral Lewis bases such as nitriles,[2a,c] mono- and dicarbonyl compounds,[2a,c,d,4] and many others (see ref 5 and papers cited therein). In the case of monocarbonyl compounds (aldehydes,[4d] ketones,[4d,e] esters,[4b] amides of carboxylic acids[4a,b]), complexes with one, two, or three Lewis basic species per one anticrown molecule are produced. All these adducts are characterized by the presence of at least one fragment wherein a basic oxygen atom of the carbonyl group is cooperatively coordinated by all Lewis acidic Hg sites of the anticrown, thereby leading to the unusual pyramidal or bipyramidal structures. The amide nitrogen atom and the oxygen atom of the ester alkoxy group do not participate in the bonding to the macrocycle. In the case of dicarbonyl compounds such as *p*-benzoquinone and maleic anhydride, 1:2 and 2:2 complexes with **1** were isolated and these adducts have double-decker sandwich structures.[4f] Here, too, only carbonyl oxygen atoms of the Lewis base are involved in the coordination with the anticrown molecules.



(**1**)

On the basis of these results, we decided to study the behavior of macrocycle **1** in reactions with typical keto−enol tautomeric

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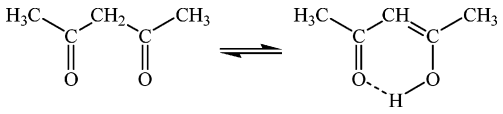
systems. Because keto and enol forms should differ from each other in the Lewis basicity of their oxygen atoms, one might assume that these differences would reflect essentially on the relative stability of the corresponding keto and enol complexes of **1** and, as a consequence, on the tautomer binding selectivity. In the present paper, data on the interaction of macrocycle **1** with the acetylacetone (AA) tautomeric system are reported.

Results and Discussion

Liquid AA is known to consist of ca. 80% of the enol form and 20% of the keto form.[6] In solutions, the enol/keto ratio can vary depending on the nature of a solvent, concentration, and temperature. In the gas phase, the content of the enol reaches 97.6%,[6] and in the crystal at 110 K, the molecules of AA exist entirely as the enol form.[7] It is known also that a number of organic hosts such as 2-ethyladenine, 1,1′-binaphthyl-2,2′-dicarboxylic acid, 1,1-di(*p*-hydroxyphenyl)cyclohexane, and some others are able to bind selectively the enol form of AA, giving rise to crystalline 1:1 or 2:2 inclusion complexes.[8] Depending on the nature of the host, hydrogen bonds or van der Waals interactions are responsible for the formation of these supramolecular aggregates.



A quite different situation is observed when macrocycle **1** reacts with the AA tautomeric system. Here, the selective binding of the less stable keto form of AA occurs and a complex, $\{[(o\text{-}C_6F_4Hg)_3]_2(AA)\}$ (**2**), containing one molecule of AA in its keto form per two anticrown molecules is produced. By using this reaction, one can totally shift the keto−enol equilibrium in AA toward its keto form stabilized by the complexation.

Complex **2** is a colorless crystalline solid stable in air. The IR spectrum of **2** exhibits the ν(C═O) band at 1679 (ms) cm^{-1}, which is shifted to lower wavenumbers in comparison with the ν_s(C═O) and ν_{as}(C═O) bands (1727 and 1707 cm^{-1}) for the free keto form of AA.[9] The IR spectrum of the uncoordinated enol form of AA is characterized by a very strong and broad absorption band at 1620−1623 cm^{-1}, which has been interpreted as the superposition of the C═O stretching and the C═C stretching coupled with the C−H in plane bending mode.[9,10] However, the IR spectrum of complex **2** shows only weak bands (at 1619 and 1584 cm^{-1}) in this region. The similar weak bands (at 1616 and 1585 cm^{-1}) belonging to the aromatic ring vibrations are present in the IR spectrum of free **1**. The ^{199}Hg NMR spectrum of **2** in THF ($[\mathbf{2}]_0 = 8 \times 10^{-2}$ mol·L^{-1}) differs only insignificantly from the spectrum of the starting macrocycle, but the addition of an excess of AA to a THF solution of **2** leads to a noticeable downfield shift of the ^{199}Hg resonance relative to that of free **1** (by 7 ppm at the AA:**2** ratio of 40:1). If AA is mixed with a 2-fold excess of **1** in CH_2Cl_2 ($[AA]_0 = 3.23 \times 10^{-3}$ mol·L^{-1}), then the subsequent removal of the solvent and washing of the resulting crystals with *n*-hexane give rise to analytically pure **2** in a 99% yield. This means that under such conditions practically the entire quantity of AA is transformed into its keto form stabilized by the coordination with the metal centers. According to the ^{1}H NMR spectra, the enol/keto ratio in a CH_2Cl_2 solution of AA (of the same concentration as in the above experiment) is 79:21. It should be noted, however, that the ^{199}Hg NMR spectrum of **2** in CH_2Cl_2 (as in THF) virtually does not differ from the spectrum of free **1**, thus suggesting that the equilibrium of the complexation of AA with **1** in CH_2Cl_2 is completely or almost completely shifted toward the starting reagents. Therefore, one may conclude that the above-described quantitative conversion of AA into its keto form coordinated with the mercury anticrown occurs at the step of the precipitation of crystals in the course of the removal of the solvent. The reaction of **1** with AA in the absence of a solvent also gives **2** in a close to quantitative yield.

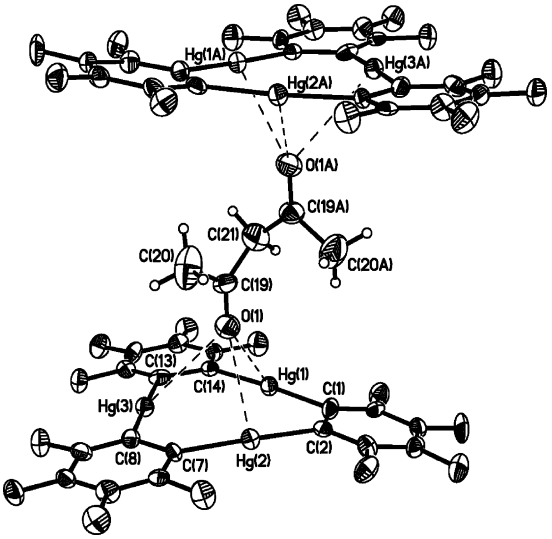


Figure 1. ORTEP representation of the molecular structure of complex **2** with thermal ellipsoids drawn at the 30% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in Complex 2

Bond Lengths			
Hg(1)−O(1)	2.989(10)	Hg(3)−C(8)	2.073(10)
Hg(2)−O(1)	3.020(10)	Hg(3)−C(13)	2.073(9)
Hg(3)−O(1)	3.198(9)	Hg(1)−C(14)	2.044(10)
Hg(1)−C(1)	2.079(10)	C(19)−O(1)	1.197(15)
Hg(2)−C(2)	2.064(11)	C(19)−C(21)	1.55(2)
Hg(2)−C(7)	2.061(9)	C(19)−C(20)	1.53(2)

Bond Angles			
C(1)−Hg(1)−C(14)	176.8(4)	O(1)−C(19)−C(21)	119.0(14)
C(2)−Hg(2)−C(7)	175.5(4)	C(20)−C(19)−C(21)	115.7(14)
C(8)−Hg(3)−C(13)	178.3(4)	C(19)−C(21)−C(19A)[a]	107(2)
O(1)−C(19)−C(20)	125.0(15)		

[a] Symmetry transformation $-x + 1, y, -z + 3/2$ was used to generate equivalent atoms.

The structure of **2** is shown in Figure 1. Selected bond lengths and angles are listed in Table 1. The complex occupies in the crystal a special position on a 2-fold axis passing through the C(21) atom and represents a double-decker sandwich wherein the molecule of AA in its keto form is disposed between the mutually parallel planes of two macrocycles and is bonded to each of these through a simultaneous coordination of its carbonyl oxygen atoms by all Hg centers of the neighboring molecule of **1**. The Hg−O distances in **2** span the range 2.989(10)−3.198(9) Å and are significantly shorter than the sum of the van der

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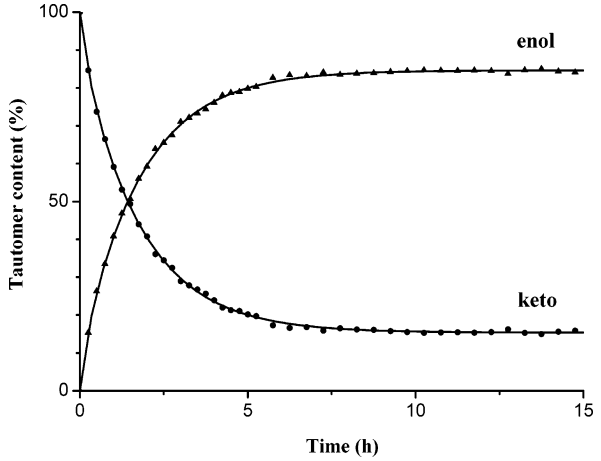

Figure 2. Kinetic curves of the transformation of the keto form of AA into the equilibrium mixture of the keto and enol forms in $CDCl_3$ at 23 °C ($[\mathbf{2}]_0 = 4.3 \times 10^{-3}$ mol·L^{-1}).

Waals radii of mercury (1.73−2.00 Å,[11a,b] 2.1 Å[11c]) and oxygen (1.5 Å,[11c] 1.54 Å[11d]) atoms. The C(19)−O(1) and C(19A)−O(1A) bond lengths (1.197(15) Å) in **2** are typical of the normal C═O double bond (av 1.23 Å), while the C(19)−C(21) and C(19A)−C(21A) distances (1.55(2) Å) are typical of the normal single C−C bond (av 1.54 Å). The carbon−oxygen framework of the coordinated AA molecule in **2** is not planar (the dihedral angle between the O(1)−C(19)−C(21) and O(1A)−C(19A)−C(21) planes is 83(1)°), and the mutual arrangement of the C═O groups corresponds to a transoid conformation (the torsion O(1)−C(19)−C(19A)−O(1A) angle is 163(2)°). The C(19)−C(21)−C(19A) bond angle is 107(2)°, thus indicating the sp^3 hybridization of the C(21) atom. Thus, the AA ligand in complex **2** exists indeed as the keto form.

The geometry of **1** does not change essentially upon the complexation. The C(19)−O(1) and C(19A)−O(1A) bond vectors in the complex are almost perpendicular to the mean planes of the central mercuracarbon rings (deviation from the normal to these planes is 7°). The mutual orientation of the macrocycles is close to a staggered conformation, and the projections of their centroids onto the plane parallel to these cycles are shifted relative to each other by 1.89 Å. The C−Hg−C bond angles in the macrocycles (175.5(4)−178.3(4)°) are close to 180°.

In a $CDCl_3$ solution (as in CH_2Cl_2), complex **2** dissociates and, as a result, the reverse transformation of the keto form of AA into the equilibrium mixture of both of its tautomers occurs (see Figure 2), which is evidenced by ^{1}H NMR spectra. The process proceeds according to a first-order equation ($k_1 = 1.32 \times 10^{-4}$ s^{-1}, $k_{-1} = 2.3 \times 10^{-5}$ s^{-1}) and reaches equilibrium after 6−7 h at 23 °C ($[\mathbf{2}]_0 = 4.3 \times 10^{-3}$ mol·L^{-1}). By that time, the relative contents of the enol and keto forms reach ca. 85 and 15%, respectively. Practically the same enol/keto ratio is observed in a solution of liquid AA in $CDCl_3$ of the same concentration. The value of the keto−enol equilibrium constant for AA, calculated from the above kinetic data ($K_e = k_1/k_{-1} = 5.74$), practically coincides with that calculated from the equilibrium concentrations of the enol and keto forms of AA ($K_e = [\text{enol}]_e/[\text{keto}]_e = 5.67$). According to the literature data,[12] the constant of the keto−enol equilibrium for AA in $CHCl_3$ at 25 °C ($[AA] = 10^{-2}$ mol·L^{-1}) determined by the HPLC method is 6.0 (enol, 85.7%; keto, 14.3%), which is close to the corresponding value (av 5.7; enol, 85%; keto, 15%; see above) found in our work.

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Conclusion

The results of our study revealed the remarkable ability of macrocycle **1** to bind selectively the less stable keto form of AA with the formation of sandwich complex **2**. The driving force of this reaction is apparently a considerably higher Lewis basicity of the carbonyl oxygen atom of the keto form of AA as compared to that of its enol form, whose C═O functionality is involved in the H-bonding to the enol hydroxide group. As a result of the formation of **2**, the keto−enol equilibrium in AA is quantitatively shifted toward its keto form stabilized by the complexation. The synthesized **2** is the first example of a structurally characterized complex containing the keto form of AA as a ligand. The described approach to stabilization of the keto form of AA by means of its complexation with an anticrown could be extended to other keto−enol equilibria wherein the keto form is the minor tautomer.

Experimental Section

General Comments. The starting macrocycle **1** was prepared according to the published procedure.[3] Commercial AA was additionally purified by distillation in vacuo. Solvents were purified by conventional methods and were distilled prior to use. The IR spectra were recorded on a Nicolet Magna 750 Series II Fourier spectrometer. The ^{199}Hg and ^{1}H NMR spectra were registered on a Bruker AMX-400 instrument. The relatative content of the keto form of AA in solutions (CD_2Cl_2 and $CDCl_3$) was determined from the intensity of the singlet of the methylene protons in the ^{1}H NMR spectra ($\delta = 3.56$ ppm in CD_2Cl_2 and 3.55 ppm in $CDCl_3$), whereas the content of the enol form was determined from the intensity of the singlet of the methyne proton ($\delta = 5.56$ ppm in CD_2Cl_2 and 5.46 ppm in $CDCl_3$).

Synthesis of {[(*o*-C$_6$F$_4$Hg)$_3$]$_2$(AA)} (2). A solution of AA (0.01 mL, 0.1 mmol) in 1 mL of CH_2Cl_2 was added to a solution of **1** (0.209 g, 0.2 mmol) in 30 mL of CH_2Cl_2, and the reaction mixture was allowed to slowly evaporate at 20 °C to dryness. After 2 days, the resulting colorless crystals of **2** were washed with *n*-hexane (2 × 2 mL) and dried in vacuo at 20 °C for 3 h. Yield of **2**: 0.218 g (99%). Anal. Calcd for $C_{41}H_8F_{24}Hg_6O_2$: C, 22.47; H, 0.37; F, 20.80. Found: C, 22.36; H, 0.33; F, 20.78. IR (Nujol mull, ν(CO), cm^{-1}): 1679 (ms). In the other experiment, macrocycle **1** (0.105 g, 0.1 mmol) was dissolved in 3 mL of AA at 20 °C, and the resulting solution was allowed to stand overnight in a closed system. After 24 h, the precipitated colorless crystals of **2** were filtered off, washed with ether (2 × 1 mL), and dried at 20 °C in vacuo for 3 h. Yield of **2**: 0.104 g (95%). Anal. Calcd for $C_{41}H_8F_{24}Hg_6O_2$: C, 22.47; H, 0.37; F, 20.80. Found: C, 22.60; H, 0.46; F, 20.93. IR (Nujol mull, ν(CO), cm^{-1}): 1679 (ms). For carrying out the X-ray diffraction study, the crystals of **2** were not dried in vacuo.

X-ray Diffraction Study of Complex 2. $C_{41}H_8F_{24}Hg_6O_2$, $M = 2192.01$, the crystals of **2** are monoclinic, space group $C2/c$, $a = 24.5187(13)$ Å, $b = 14.2738(7)$ Å, $c = 13.8951(7)$ Å, $\beta = 116.712(1)°$, $V = 4344.0(4)$ Å^3, $T = 260$ K, $Z = 4$, μ(Mo Kα) = 21.269 mm^{-1}, crystal size 0.30 × 0.25 × 0.05 mm. The single-crystal X-ray diffraction experiment was carried out with a Bruker SMART 1000 CCD diffratometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å, ω-scan, $2\theta < 60°$) at 260 K. Reflection intensities were integrated with the use of SAINT software,[13] and the semiempirical method SADABS[14] was applied for absorption correction ($T_{min}/T_{max} = 0.080/0.333$). A total of 22 109 reflections were measured, and 6284 ($R_{int} = 0.0594$) independent reflections

were used in further calculations and refinement. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 in anisotropic (for non-hydrogen atoms) approximation. Hydrogen atoms were placed geometrically and included in the structure factor calculation in the riding motion approximation. The final refinement was converged to $R_1(F) = 0.0486$ (for 3941 observed reflections with $I > 2\sigma(I)$) and $wR_2(F^2) = 0.1018$ (for all unique reflections), GOF = 1.036; the number of refined parameters is 331. All calculations were performed on an IBM PC/AT using SHELXTL software.[15]

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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