partame is close to 90° from the zwitterionic ring of the aspartic acid though the two rings are not coplanar as we find for the sweet compounds reported here. This slight twisting of the phenyl ring could be due to the packing forces within the crystal structure. The flexibility of aspartame in solution would easily allow for rotation about the ϕ bond to a conformation in which the rings are coplanar. Figure 2 shows our model with this structure of aspartame superimposed.

We are presently carrying out X-ray diffraction studies of the four analogues. The structure of the two retro-inverso analogues which cocrystallize has been solved and will be reported elsewhere.[7] The crystal structures have molecular topologies quite similar to those shown in Figure 1 for the retro-inverso analogues. There are slight conformational differences that can be obtained by rotations about ϕ and ϕ'.

In summary, low-energy conformations of the four constrained stereoisomeric analogues were chosen from several different minima generated from minimum energy calculations on the basis of agreement with NMR data. By utilizing these conformations we are able to generate a model to explain the differing tastes of the analogues. Our model, though similar to those proposed by Temussi[8,9] and van der Heijden,[10] employs a different orientation of the AH–B and X groups.[11,12] We are therefore able to correlate the structures of the stereoisomeric compounds with taste. We are now examining results from computer simulations, X-ray crystallographic structures, and NMR studies of a wide variety of amino acid- and peptide-based tastants to establish the generality of our model and to develop a model for the bitter taste.

Acknowledgment. We acknowledge the support of the National Institute of Dental Research (DE-05476). One of us (D.F.M.) would like to acknowledge a fellowship from the Upjohn Corp.

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Multidentate Lewis Acids. Complex of a Macrocyclic Tetradentate Organomercuric Perfluoroglutarate[†]

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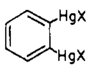
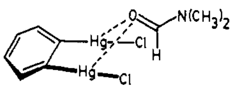
Well-designed bidentate Lewis acids can recognize and bind simple anions and basic sites in organic molecules.[1,2] For example, 1,2-phenylenedichlorodimercury (**1**) forms a 2:1 complex with chloride in which the added chloride occupies an electrophilic cavity created by four atoms of mercury.[1b,d] In addition, structure **4** shows how the mercury atoms of dichloride **1** can cooperate to bind dimethylformamide.[1a] Similar complexation of thiocarbonyl compounds by bis(trifluoroacetate) **2** leads to useful chemical activation of the carbon–sulfur double bond.[1c] The unusual coordination chemistry of simple bidentate Lewis acids like compounds **1** and **2** made us eager to study complex, cyclic Lewis acids containing a larger number of well-oriented electrophilic sites.[3] This communication describes the first synthesis and structural characterization of a complex of a macrocyclic multidentate Lewis acid.



1 (X = Cl)
2 (X = OOCCF$_3$)
3 (X = OOCCH$_3$)



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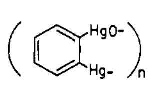

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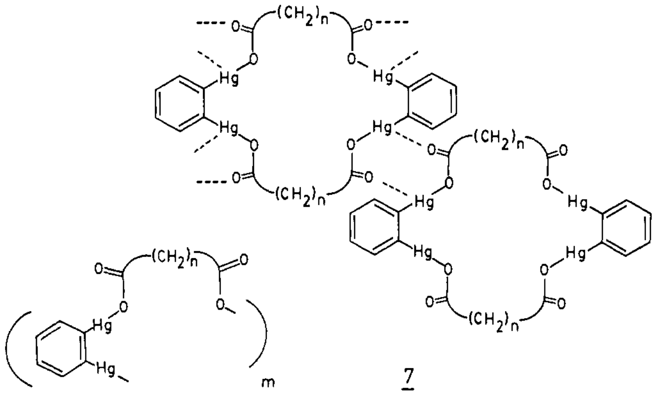
Treatment of dichloride **1** with aqueous NaOH produces (μ-1,2-phenylene-μ-oxo)dimercury (**5**), a polymeric oxide that can be converted into carboxylates like bis(trifluoroacetate) **2** and diacetate **3** by treatment with 2 equiv of the appropriate carboxylic acid.[1c] We therefore hoped that similar reactions with α,ω-dicarboxylic acids would yield macrocycles containing 1,2-phenylenedimercury units linked by dicarboxylate bridges. Treatment of suspensions of oxide **5** in THF with dilute solutions (0.007 M) of a wide variety of dicarboxylic acids produced a series of dicarboxylates that showed low crystallinity and negligible solubility in THF, CH$_3$CN, and Me$_2$SO. Although these intractable materials could not be characterized in detail, we believe that they are linear polymers **6** or polymeric aggregates of multidentate macrocyclic oligomers represented arbitrarily by the cyclic dimers of structure **7**. The large number of potential intermolecular carboxylate bridges in the aggregates would account for their extremely low solubility, which is characteristic even of simple bidentate carboxylates like diacetate **3**.



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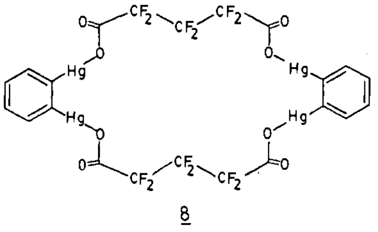
7

Since bis(trifluoroacetate) **2** is significantly more soluble and more Lewis acidic than diacetate **3**, we treated oxide **5** with an equimolar amount of perfluorosuccinic acid. Unfortunately, the extremely low solubility of the final product in THF, CH$_3$CN, and Me$_2$SO suggested that it was a linear polymer. In contrast, the reaction of oxide **5** in THF with an equimolar amount of perfluoroglutaric acid produced a crystalline THF complex of tetradentate macrocycle **8** in 81% yield.[4]



8

[†] This paper is dedicated to Professor Henry G. Kuivila on the occasion of his 70th birthday.

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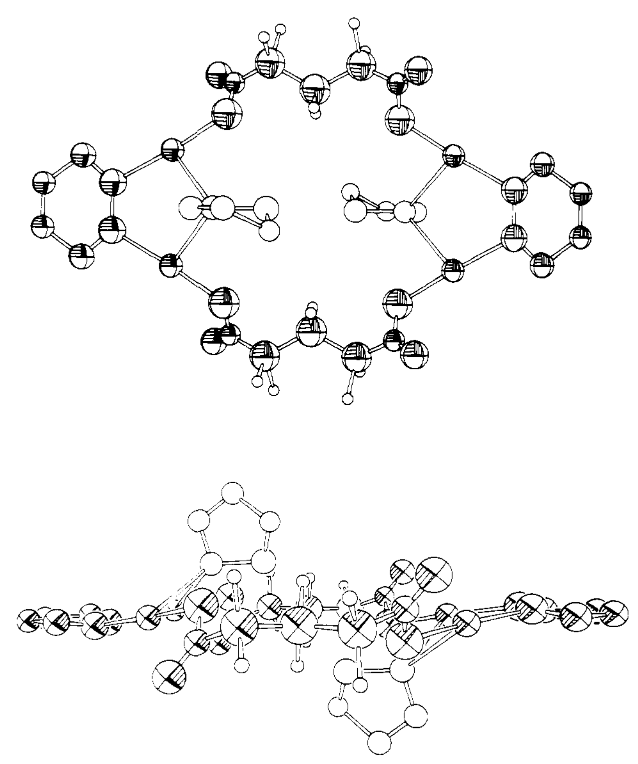

Figure 1. Two views of the structure of the 2:1 complex of perfluoroglutarate **8** with tetrahydrofuran. Fluorine atoms are represented by spheres of arbitrary size, and all hydrogen atoms are omitted for clarity.

An X-ray crystallographic study of this complex has revealed that its unit cell contains the 2:1 structure shown in Figure 1 and a second, closely related 6:1 motif.[5] In both complexes, the macrocyclic 22-membered ring of perfluoroglutarate **8** is approximately planar and surrounds a hole nearly 12 Å long and 7 Å wide. In the 2:1 complex, the oxygen atom of each THF molecule interacts symmetrically with the mercury atoms of a 1,2-phenylenedimercury unit, and one THF is bound above the plane of the macrocyclic ring while the other lies below. In the 6:1 complex, two molecules of THF are bound above the macrocyclic ring by similar interactions and two are bound below. The additional molecules of THF interact outside the ring with individual atoms of mercury. Both structures obey two rules generally followed by complexes of Hg(II): mercury forms two strong collinear primary bonds, and it retains appreciable acidity in the plane perpendicular to these primary bonds, allowing secondary coordination. Thus the endocyclic C–Hg–O angle in the 2:1 complex is 174 (2)°, and the C–Hg–O angle involving the oxygen atom of THF is 100 (2)°. Other angles and distances are similar to those found in related derivatives of 1,2-phenylenedimercury[1] and in phenylmercuric trifluoroacetate.[6]

Of special importance is the distance from mercury to the coordinated oxygen of THF, which is 2.85 (4) Å in the 2:1 complex. Since the van der Waals radii of oxygen and mercury are approximately 1.4 and 1.5–1.73 Å,[7,8] respectively, the mercury–oxygen interactions in the complexes are moderately strong. As a result, the bound molecules of THF resist elimination during drying at 25 °C/0.1 Torr. Nevertheless, all are displaced when a better Lewis base like bidentate dimethoxyethane is added. The particular orientation of the four strongly electrophilic sites in perfluoroglutarate **8** should make it ideal for the recognition and selective binding of molecules containing two basic sites separated by about 7 Å.

The remarkably efficient formation of the large ring of perfluoroglutarate **8** is a consequence of the rigidity of the 1,2-phenylenedimercury units, the collinearity of primary bonds to mercury, and the favorable dimensions and conformation of perfluoroglutarate bridges. Perfluorosuccinate bridges may be too short to allow a similar macrocyclization, and the antiperiplanar orientation of carboxylate groups normally preferred by perfluorosuccinates may be an additional disadvantage.[9]

Constructing macrocyclic multidentate Lewis acids by using perfluorodicarboxylate bridges to link strongly electrophilic sites is a simple, powerful, and potentially general strategy. Study of the structure and coordination chemistry of these macrocyclic multidentate Lewis acids should be richly rewarding.

Acknowledgment. This work was financially supported by the Natural Sciences and Engineering Research Council of Canada and the Ministère de l'Éducation du Québec. We thank Robert Mayer for recording our ^{199}Hg NMR spectra.

Supplementary Material Available: Spectroscopic and analytical data for the THF complex of perfluoroglutarate **8**, description of the crystal structure, and tables of bond distances and angles and of atomic positional and thermal parameters (12 pages). Ordering information is given on any current masthead page.

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(4) The structure assigned to this complex is consistent with its elemental analysis and its IR, ^{1}H NMR, and ^{199}Hg NMR spectra. These data are included in the supplementary material.

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Formation, Chemistry, and Thermochemistry of Primary Amide Complexes of Fe$^+$ and Co$^+$ in the Gas Phase

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Recently there has been renewed interest in the preparation and properties of transition-metal–amide complexes.[1,2] Later transition-metal amides may have catalytic utility in the synthesis of amines and other nitrogen-containing organic compounds[3] but to date very few have been reported. The instability of these complexes has been attributed to the unfavorable d ← p interaction for later transition metals.[1a] Because of this, the majority of the amide complexes reported have contained α-nitrogen groups such as SiR$_3$ which can withdraw $p\pi$ electron density from the nitrogen and thus stabilize the M–N bond.

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