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Coordination Chemistry Reviews
145 (1995) 55–73

COORDINATION CHEMISTRY REVIEWS

Multiple coordination of carbonyl compounds by multidentate main group Lewis acids

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Received 29 September 1994; accepted 31 October 1994

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Abstract

Similar to crown ethers and other multidentate Lewis bases, multidentate Lewis acids have unique features that promise to give them broad utility in chemistry. In particular, they can be designed so that their multiple sites of Lewis acidity are able to interact simultaneously with basic sites in guest molecules, so leading to recognition, binding and chemical activation of the guest. Of special interest to the organic chemist is the possibility of devising multidentate maingroup Lewis acids able to enhance the reactivity of carbonyl compounds by multiple coordination of the basic carbonyl oxygen atom. Our work has established that carbonyl oxygen atoms are actually basic enough to accommodate two or more sites of Lewis acidity at the same time — at least when the electrophilic sites are joined together to create geometrically complementary multidentate Lewis acids. Specifically, we have shown that bidentate and tetradentate Lewis acids derived from 1,2-phenylenedimercury can form remarkable adducts with amides in which the carbonyl oxygen atom interacts simultaneously with as many as four sites of Lewis acidity. Furthermore, changes in the geometry and spectroscopic properties

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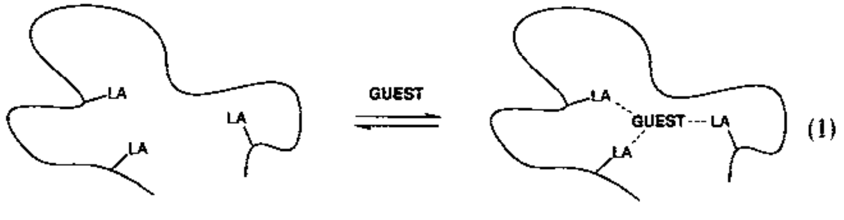
SSDI 0010-8545(95)09103-3

of the bound amides provide strong evidence that multiple coordination can lead to enhanced reactivity of the C=O double bond.

Keywords: Multidentate Lewis acids

1. Introduction

An intriguing subject of contemporary research in main-group coordination chemistry is the study of complex reagents **1** that hold multiple sites of Lewis acidity (LA) in well-defined orientations [1–8]. (For recent related studies of multidentate main-group Lewis acids, see Ref. [83].) These multidentate Lewis acids are interesting because they can be designed to recognize, bind and chemically activate guests that have a complementary arrangement of basic sites, (Eq. (1)).



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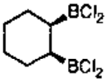
The first systematic study of the synthesis and coordination chemistry of multidentate Lewis acids was published in 1966 by Shriver and Biallas [2]. This study and subsequent publications by the same group described a series of novel bidentate Lewis acids containing boron, including the representative diborane (**2**)



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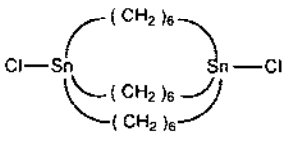
and provided important preliminary information about the ability of the adjacent electrophilic sites in these structures to interact simultaneously with basic sites in guest molecules.

Curiously, this pioneering work did not immediately draw other chemists to the field and challenge them to devise new multidentate main-group Lewis acids. Eventually, however, the initial research of Shriver and Biallas inspired other chemists to study a rich variety of molecules in which multiple sites of LA are held in specific orientations designed to favor the selective complexation of complementary basic guests. Particularly noteworthy examples include the macrobicyclic bidentate Lewis acid **3** and related cyclic and acyclic multidentate stannanes reported by Newcomb and coworkers [3] and Kuivila and coworkers [4], 1,8-bis(dichloroboryl)naphthalene (**4**) and similar bidentate systems studied by Katz [5], the macrocyclic trisilane **5** described by Jung and Xia [6], the macrocyclic tetradentate organomercuric perfluoroglutarate **6** and similar structures reported by Wuest [1c,1d], and the macrocyclic tetradentate Lewis acid **7** and related compounds described by Hawthorne and coworkers [7], in which multiple electrophilic atoms of mercury are linked by carborane units.

No chemist with an active sense of aesthetics can fail to be impressed by the beauty and structural variety of compounds **2**–**7**. Unfortunately, these compounds and their relatives are typically difficult to synthesize, and they remain exotic curiosities of the laboratory; moreover, their unusual structural features and characteristic abilities to bind basic guests have not yet found applications of genuine practical value in molecular recognition, transport, catalysis or other areas of chemistry. Although studies of multidentate Lewis acids have had an undeniable conceptual



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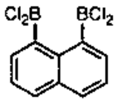

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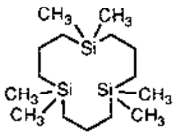

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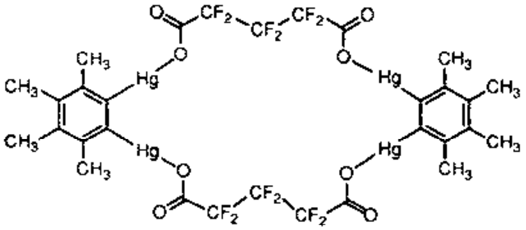

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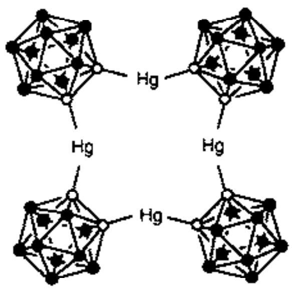

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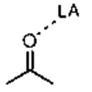
influence, potential practical benefits have been neglected and no truly useful reagents have emerged. As a result, multidentate Lewis acids have not yet achieved prominence in chemistry, unlike multidentate Lewis bases such as crown ethers. Therefore, we have begun a sustained effort to identify unique features of multidentate Lewis acids that might allow them to play a broader role in chemistry, particularly as catalytic or stoichiometric reagents in organic synthesis.

Simple monodentate Lewis acids are useful to the synthetic organic chemist, because their interaction with basic sites in organic molecules can facilitate subsequent reactions. For example, the intrinsically high reactivity of carbonyl compounds can be enhanced by forming complexes **8** with monodentate Lewis acids [9]. Complexation reduces the electron density on the carbonyl carbon, further polarizes the C—O bond, lowers the energy of the lowest unoccupied molecular orbital (LUMO) [10] and, thus, can have dramatic kinetic affects. A typical example is provided by the Diels–Alder reaction of methyl acrylate with butadiene at 20 °C in benzene, which is 10^5 times faster in the presence of an equimolar amount of $AlCl_3$ [11]. Simultaneously, Lewis acids can also have notable effects on regiochemical and stereochemical selectivities. For all these reasons, simple Lewis acids play a major role as catalysts and stoichiometric reagents in contemporary organic synthesis.



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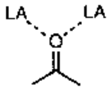

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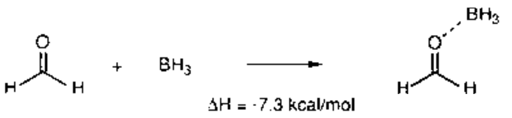
The precise geometries of adducts **8** show substantial variability; in general, however, neutral main-group Lewis acids favor $\eta^1(\sigma)$ complexes in which the Lewis acid lies close to the carbonyl plane along the direction of one of the formal sp^2 lone pairs on oxygen [9]. (For comparisons of $\eta^1(\sigma)$ and $\eta^2(\pi)$ bonding of carbonyl compounds by Lewis acids, see Ref. [12].) In principle, this leaves the other sp^2 lone pair free and available for binding a second equivalent of Lewis acid, so producing termolecular doubly coordinated complexes **9**. Such adducts, as well as even more highly coordinated analogues, should take fuller advantage of the electron density on oxygen and should experience supplementary electrophilic activation, making them still more susceptible to further reactions. (Similar doubly coordinated complexes have been postulated as activated intermediates or transition states in additions of organometallic reagents to carbonyl compounds [13].)

Unfortunately, the assembly of termolecular adducts **9** from carbonyl compounds and two independent Lewis acids is entropically unfavorable; moreover, it is by no means obvious that normal carbonyl compounds are basic enough to accommodate two Lewis acids at the same time. Indeed, there are no known termolecular complexes in which two or more main-group Lewis acids interact simultaneously with the carbonyl oxygen atom of a ketone or an aldehyde. However, the following observations suggest that the formation of such complexes may nevertheless be enthalpically feasible.

For example, it is well known that carbonyl oxygen atoms can accept multiple hydrogen bonds at the same time (a dramatic example is the carbonyl oxygen atom of crystalline urea, which accepts four hydrogen bonds [14]), and evidence has been presented to suggest that double hydrogen bonding has a measurable effect on reactivity. (For a measure of the effect of double hydrogen bonding on the reactivity of carbonyl compounds, see Ref. [15a]. For related studies of doubly protonated carbonyl compounds, see Ref. [15b].) In addition, a small number of crystal structures can be found in which the carbonyl oxygen atoms of particularly basic carbonyl compounds interact with two alkali metal cations, at least in the solid state [16,17]. Further evidence that the double coordination of simple carbonyl compounds by main-group Lewis acids is enthalpically feasible is provided by ab initio calculations at the 6-31G* level reported by Wiberg and Lepage [18]. They determined that the binding of one equivalent of BH_3 by formaldehyde (Eq. (2)) should be markedly exothermic ($\Delta H = -7.3$ kcal mol^{-1}) and that further reaction of the 1 : 1 adduct with a second equivalent of BH_3 (Eq. (3)) should be less favorable, but still modestly exothermic ($\Delta H = -2.3$ kcal mol^{-1}). If we assume that ΔS for each step is approximately -38 eu [19] and that the values of ΔH calculated for the gas phase can be applied to selected condensed phases, then a solution initially 1 M in formaldehyde and 2 M in BH_3 will consist (at equilibrium) of approximately 90% of the 1 : 1 adduct and only 0.0004% of the 1 : 2 adduct at -100 °C. Under these conditions, the 1 : 2 adduct would have to be at least 10^5 times more highly activated than the 1 : 1 adduct to have a kinetically significant effect on the reactions of formaldehyde. Although the 1 : 1 adduct may actually be 10^5 times more reactive than uncomplexed formaldehyde, further activation of this magnitude in the 1 : 2 adduct is unlikely. It is true that somewhat higher percentages of 1 : 2 adducts could presumably be generated by using boron halides, which are stronger Lewis acids than BH_3 [20,21]. Even



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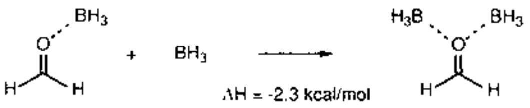

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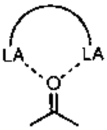
under the best circumstances, however, termolecular 1 : 2 adducts will not be present in high concentrations and it will be difficult to put their potential activation to effective use.

To make doubly coordinated adducts of carbonyl compounds chemically accessible, the two sites of Lewis acidity should be linked together to create a single bidentate unit. If the bidentate Lewis acid is well designed, the formation of significant amounts of the bimolecular complex **10** may then be both enthalpically and entropically feasible. For example, if ΔH and ΔS for the formation of the bimolecular singly coordinated adduct **11** of formaldehyde and a rigid bidentate boron hydride are -7.3 kcal mol^{-1} and -38 eu, respectively; if ΔH and ΔS for the subsequent formation of the bimolecular doubly coordinated adduct **12** are -2.3 kcal mol^{-1} and -9 eu [19], then a solution initially containing 1 M concentrations of formaldehyde and the bidentate boron hydride should consist (at equilibrium) of 10% of adduct **11** and 89% of adduct **12** at -100 °C. Even higher percentages of doubly coordinated adducts could presumably be prepared by using bidentate boron halides. *This suggests that bimolecular doubly coordinated adducts* **10** *may be able to play kinetically dominant roles in organic reactions, even if their reactivity is merely equal to that of the singly coordinated analogues* **8**.

In addition, bidentate Lewis acids have other features that promise to make them broadly useful in organic synthesis. In certain cases, singly coordinated adducts **8** that are formed using stoichiometric or catalytic amounts of chiral non-racemic monodentate Lewis acids can react with high degrees of enantioselectivity [22]; in general, however, enantioselectivities in such reactions are low, because rotation around the dative oxygen–Lewis acid bond can occur to give a complex mixture of reactive conformers. Related adducts **10** derived from chiral non-racemic bidentate Lewis acids may prove to be much more suitable for promoting enantioselective reactions, since double coordination imposes additional conformational constraints. It is also important to note that, although our analysis has focused on the chemical activation of carbonyl compounds, bidentate Lewis acids can also be designed to recognize and bind basic sites in many other types of molecule, so forming novel complexes with enhanced reactivity. For example, ethers can be expected to form activated adducts **13**



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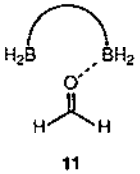

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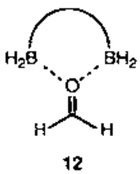

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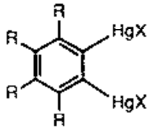
when treated with suitable bidentate Lewis acids [1c,1d]. For all these reasons, we are optimistic that a systematic study of multidentate Lewis acids will provide organic chemists with useful new tools.

2. Double coordination of amides by bidentate Lewis acids derived from 1,2-phenylenedimercury

Although doubly coordinated complexes **10** of carbonyl compounds and bidentate main-group Lewis acids promise to have properties of significant chemical interest, evidence that such adducts can exist remained weak and circumstantial for many years, but detailed studies of their structure and reactivity have recently begun to appear. In an earlier study [1g], we noted that 1,2-phenylenebis(trifluoroacetato-O)-dimercury (**14**),



14 ($R = H, X = OOCCF_3$)
15 ($R = H, X = Cl$)
18 ($R = CH_3, X = OOCCF_3$)
20 ($R = H, X = OOCCF_3$)
25 ($R = CH_3, X = OSO_2CF_3$)
26 ($R = CH_3, X = Cl$)

a bidentate Lewis acid, binds thioketones to form complexes particularly susceptible to subsequent reactions, including hydrolysis and reductive desulfurization. Similar reactions of thioketones in the presence of two molar equivalents of phenylmercuric trifluoroacetate — a monodentate analogue — yielded different products, suggesting that double coordination of the sulfur atom of thiocarbonyl compounds by bidentate reagent **14** may occur and may exert special chemical effects.

In the course of studying related derivatives of 1,2-phenylenedimercury, we found that dichloride **15** forms a crystalline 1:1 adduct with dimethylformamide. This observation intrigued us, since organomercuric chlorides do not normally form stable adducts of this type. In 1982, Grdenic et al. reported the structure of a stable 1:1 adduct of dimethylformamide and $(ClHg)_3CCHO$, which contains three electrophilic atoms of mercury [23]. One interacts strongly with the carbonyl oxygen atom of dimethylformamide to form a dative Hg—O bond with a length of 2.75(5) Å, and a second interacts weakly to form an Hg—O bond with a length of 3.03(6) Å, which is very close to the sum of the van der Waals radii [24,25]. The structure of the adduct was therefore determined by X-ray crystallography and is shown in Fig. 1, along with selected bond lengths and angles [1e]. The carbonyl oxygen atom

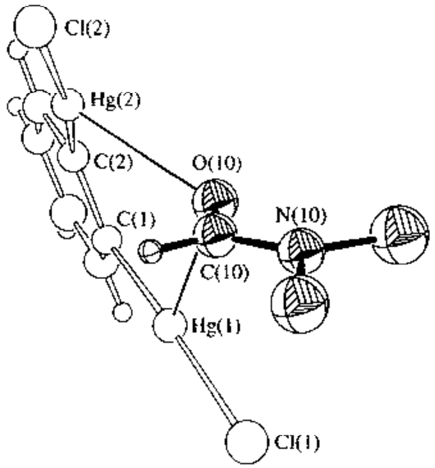


Fig. 1. ORTEP drawing of the structure of 1:1 complex of dimethylformamide with dichloro-1,2-phenylenedimercury (**15**). The formyl hydrogen atom of dimethylformamide and all atoms of dichloride **15** appear as spheres of arbitrary size and other hydrogen atoms are omitted for simplicity. Other atoms are represented by ellipsoids corresponding to 50% probability. Selected bond lengths include the following: Hg(1)—C(1) = 2.047(16); Hg(2)—C(2) = 2.044(16); Hg(1)—Cl(1) = 2.334(5); Hg(2)—Cl(2) = 2.346(4); Hg(1)—O(10) = 2.777(13); Hg(2)—O(10) = 2.681(13); C(10)—O(10) = 1.26(2); C(10)—N(10) = 1.31(2) (all in ångströms). Selected angles include the following: C(1)—Hg(1)—Cl(1) = 176.6(4)°; C(2)—Hg(2)—Cl(2) = 171.5(5)°; C(10)—O(10)—Hg(1) = 116(1)°; C(10)—O(10)—Hg(2) = 120(1)°; N(10)—C(10)—O(10)—Hg(1) = 109(2)°; N(10)—C(10)—O(10)—Hg(2) = −152(2)°.

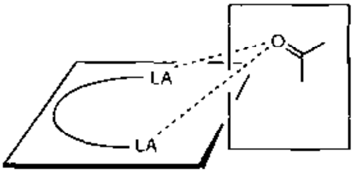
interacts simultaneously and almost symmetrically with both Lewis acidic atoms of mercury, and the average length of the dative Hg—O bonds (2.73(1) Å) is significantly shorter than the sum of the van der Waals radii of oxygen (1.40 Å) [24] and mercury (1.73 Å) [25]. This complex is noteworthy, because it provided the first unambiguous evidence that the two electrophilic sites in suitably designed bidentate Lewis acids can interact simultaneously with the oxygen atom of carbonyl compounds.

The unique double coordination of dimethylformamide presumably explains the abnormally high stability of the complex; nevertheless, the Lewis acidity of organomercuric chlorides is inherently weak and crystals of the adduct slowly lose dimethylformamide under vacuum. Less basic carbonyl compounds such as ketones, do not form isolable complexes of any kind, and the solubility of dichloride **15** is too low to permit studies of the stoichiometry or thermodynamics of complexation in solution. It is interesting to note that, even though the carbonyl oxygen atom is shared by two sites of Lewis acidity, the individual dative Hg—O bonds are not significantly longer than those in related singly coordinated adducts of mercuric halides [23–26]. Furthermore, there is no evidence that the unusual coordination of dimethylformamide by bidentate dichloride **15** is strong enough to cause major structural changes in the host or the guest. For example, the average Hg—C bond length (2.046(16) Å) and Hg—Cl bond length (2.340(5) Å) are normal [27], and the average C—Hg—Cl angle (174.0(5)°) remains close to 180°.

Unfortunately, the standard deviations in the structural parameters of the bound amide, including the carbonyl C—O bond length (1.26(2) Å) and the N—C(O) bond length (1.31(2) Å), are too high to permit detailed comparison with the corresponding values for uncomplexed tertiary amides [17,28a]. (For structural studies of free tertiary formamides, see Ref. [28b].) Amides are resistant to structural deformation [29], so the changes in geometric parameters induced by double coordination to a weak bidentate Lewis acid may simply be too small to be observed in a crystallographic study with relatively high standard deviations. Unambiguous evidence that the C=O double bond of dimethylformamide is weakened by double coordination is provided by IR spectroscopy, which shows that the carbonyl band at 1670 cm^{-1} in free dimethylformamide (neat liquid) shifts to 1655 cm^{-1} in the adduct (KBr).

These observations are important, because they demonstrate that carbonyl oxygen atoms can be basic enough to accommodate two sites of Lewis acidity at the same time — at least when the electrophilic sites are joined together to create a single geometrically complementary bidentate Lewis acid. Moreover, double electrophilic coordination can cause C=O double bonds to become weaker, and presumably longer, making them more susceptible to subsequent reactions.

The marked tendency of main-group Lewis acids to form $\eta^1(\sigma)$ adducts **8** with carbonyl compounds suggests that both sites of Lewis acidity in doubly coordinated adducts **10** should lie close to the carbonyl plane. However, Fig. 1 shows that the 1:1 adduct of dimethylformamide with bidentate mercuric chloride **15** deviates dramatically from this expectation. In fact, the complexation can be more accurately described as a three-center, two-electron bonding arrangement (**16**) in which the host and guest lie in nearly perpendicular planes.



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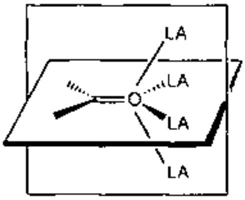

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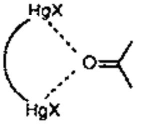
The carbonyl oxygen atom can be considered to provide a single lone pair, and the two atoms of mercury each contribute an empty orbital. Alternatively, the bonding can be described as a hybrid of $\eta^1(\sigma)$ and $\eta^2(\pi)$ interactions. The observed orientation may be favored because it allows both atoms of mercury to remain syn to the formyl hydrogen, so avoiding the larger $N(CH_3)_2$ group. It may also be a simple geometric consequence of the particular orientation of the two electrophilic atoms of mercury in bidentate Lewis acid **15** and their characteristic tendency to accept coordinative interactions in a plane perpendicular to the collinear primary bonds to carbon and chlorine [30]. The formation of an $\eta^1(\sigma)$ adduct with a coplanar orientation of host and guest is disfavored, because it cannot respect the preference for orthogonal coordination and simultaneously accommodate dative Hg···O bonds of normal length to the carbonyl oxygen atom of dimethylformamide. For these reasons, we doubt that the preference of the 1 : 1 complex of dimethylformamide and bidentate Lewis acid **15** for structure **16** illustrates a general principle. More nearly coplanar arrangements (**10**) are likely to be favored in other adducts of main-group bidentate acids, although substantial deviations of the electrophilic sites from the carbonyl plane are possible.

3. Quadruple coordination of amides by bidentate Lewis acids derived from 1,2-phenylenedimercury

Adduct **16** results from the use of only one of the two formal lone pairs of the carbonyl oxygen atom of dimethylformamide, so the second lone pair remains free and available for further complexation. Therefore it is not unrealistic to imagine related adducts (**17**) in which the carbonyl oxygen atom is surrounded by four electrophilic sites provided by a pair of bidentate Lewis acids. In fact, remarkable structures of this type can be made by using 3,4,5,6-tetramethyl-1,2-phenylenebis(trifluoroacetato-O)dimercury (**18**) [1c], which is a stronger Lewis acid than the corresponding dichloride **15**. Compound **18** is also easier to make, since the treatment of 1,2,3,4-tetramethylbenzene with $Hg(OOCCF_3)_2$ provides bis(trifluoroacetate) **18** directly in high yield [1c]. The crystallization of compound **18** from dimethylformamide or diethylformamide produces complexes in which the bidentate Lewis acid and amide are present in a 2 : 3 molar ratio. The structures of the adducts were determined by X-ray crystallography and proved to be very similar; the structure of the diethylformamide complex is illustrated in Figs. 2 and 3, along with selected bond lengths and angles.

Two of the three bound amides are complexed in the normal manner; i.e. each carbonyl oxygen atom interacts with two Lewis acidic atoms of mercury derived from a single molecule of bis(trifluoroacetate) **18**, producing the same bimolecular motif **19** that is favored by the 1 : 1 complex of dichloride **15** with dimethylformamide. The lengths of the dative Hg—O bonds, which vary only within the narrow range 2.64(2)–2.82(2) Å, are similar to those found in the adduct of dichloride **15** and in related complexes [23,26]. Again, the unusual coordination of diethylformamide does not appear to cause major structural changes in the host or the guest. In particular, mercury retains two essentially collinear primary bonds and continues to accept coordinative interactions in the plane perpendicular to these bonds; in addition, the average lengths of the primary Hg—O and Hg—C bonds (2.10(2) and 2.06(3) Å respectively) are similar to those in the closely related uncomplexed bis(trifluoroacetate) **20** [31].



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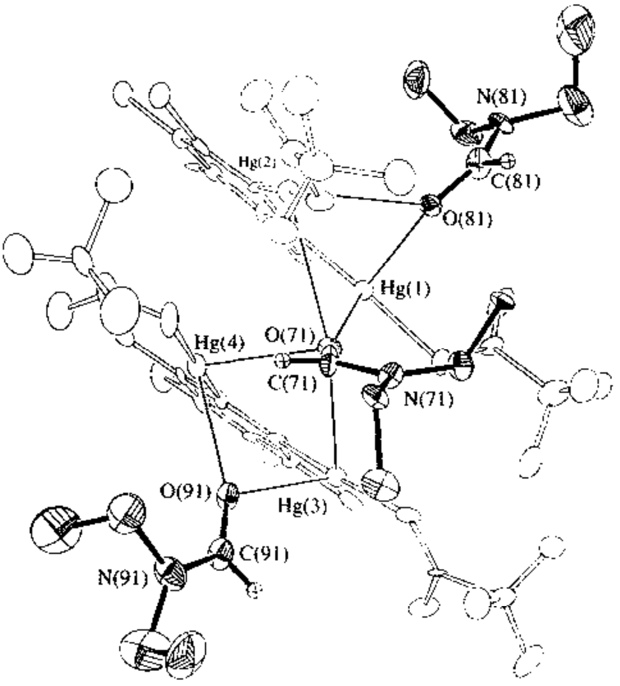


Fig. 2. ORTEP drawing of the structure of the 2:3 complex of bis(trifluoroacetate) **18** with diethylformamide. The formyl hydrogens appear as spheres of arbitrary size and other hydrogen atoms are omitted for simplicity. Other atoms are represented by ellipsoids corresponding to 30% probability. Selected bond lengths include the following: C(71)—O(71) = 1.25(5); C(81)—O(81) = 1.19(4); C(91)—O(91) = 1.19(4); C(71)—N(71) = 1.33(4); C(81)—N(81) = 1.31(4); C(91)—N(91) = 1.28(5) (all in ångströms). Other geometric parameters appear in Fig. 3.

The common tendency of bidentate dichloride **15** and bis(trifluoroacetate) **18** to form adducts **19** indicates that the 1,2-phenylenedimercury framework holds two sites of Lewis acidity in an orientation particularly well suited for the double coordination of carbonyl compounds. Although general motif **19** is favored by both bidentate Lewis acids, close comparison of Fig. 1 with Figs. 3(a) and 3(b) reveals substantial differences in the angular distributions of the Lewis acidic atoms of mercury relative to the carbonyl plane of the guest. These differences suggest that carbonyl oxygen atoms do not have very strong steric or electronic preferences for forming bonds to mercury along specific directions [18]. We conclude that the carbonyl O ··· Hg interactions have a significant electrostatic component. However, the data in Figs. 1, 3(a) and 3(b) also provide evidence for an important covalent component as well, since the shortest dative Hg—O bonds are those that lie closest to the carbonyl plane, in the direction of the carbonyl lone pairs.

The most remarkable feature of the structure of the 2:3 complex of bis(trifluoroacetate) **18** with diethylformamide is the binding of the third amide (Fig. 2). Its oxygen atom interacts simultaneously with four Lewis acidic atoms of mercury derived from two independent 1,2-phenylenedimercury units, creating the unprece-

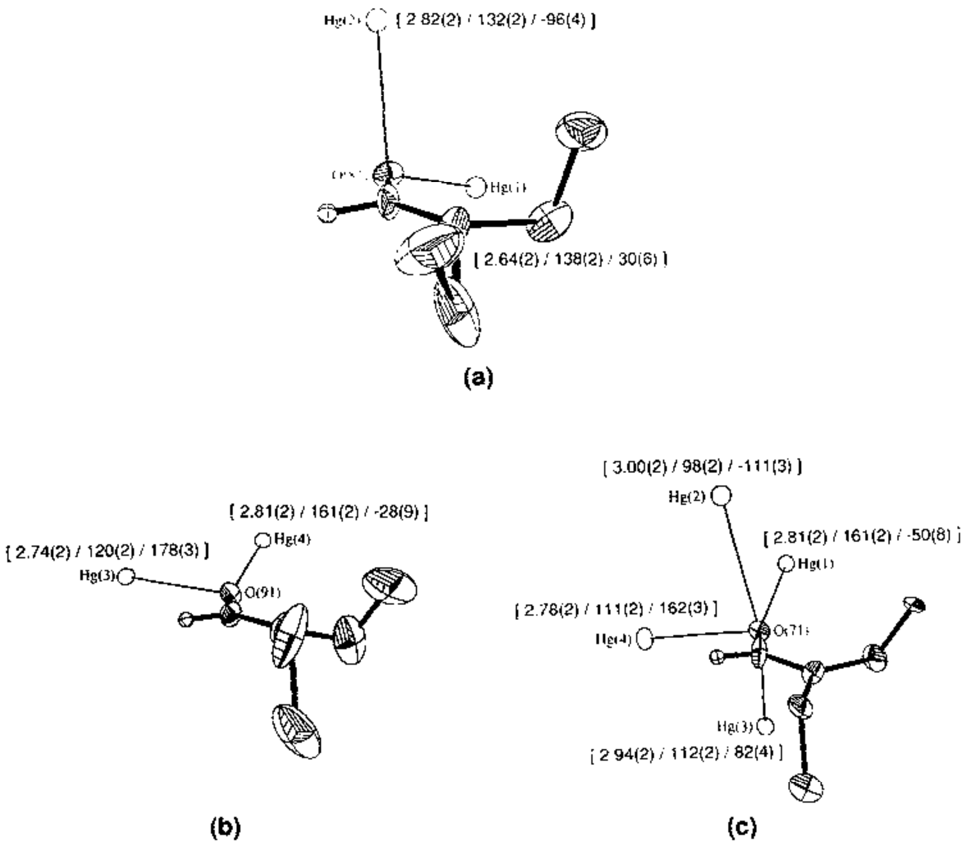
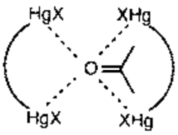


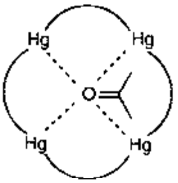
Fig. 3. ORTEP drawings of the structure of the 2:3 complex of bis(trifluoroacetate) **18** with diethylformamide, showing only the three bound amides and the associated atoms of mercury. To facilitate comparison, each structure is viewed along the carbonyl C=O axis, from slightly above the carbonyl plane. The three geometric parameters that appear next to each mercury atom correspond to the carbonyl O ··· Hg distance (Å), the C=O ··· Hg angle (degrees) and the N−C=O ··· Hg dihedral angle (degrees). The formyl hydrogens appear as spheres of arbitrary size and other hydrogen atoms are omitted for simplicity. Other atoms are represented by ellipsoids corresponding to 30% probability.

dented termolecular motif **21**. Fig. 3(c) provides a simplified structural drawing, showing only the quadruply coordinated amide and the four associated atoms of mercury. All four dative Hg−O distances are significantly shorter than the sum of the van der Waals radii of oxygen (1.40 Å) [24] and mercury (1.73 Å) [25]. Each 1,2-phenylenedimercury unit forms one short and one longer dative Hg−O bond to the carbonyl oxygen atom of the quadruply coordinated diethylformamide. The two shortest bonds are those that lie closest to the carbonyl plane, and the two longest lie in an approximately orthogonal plane.

In principle, quadruple coordination of an amide should have a marked effect on its structure, spectroscopic properties and reactivity. Unfortunately, the standard



21



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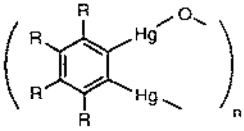
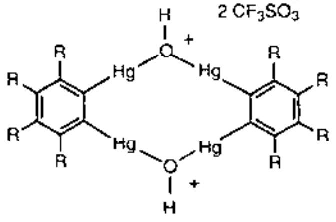
deviations in the structural parameters are too great to permit detailed comparison of the three bound amides, and we cannot confirm that the carbonyl C−O and N−C(O) distances in the quadruply coordinated amide are significantly longer and shorter, respectively, than those in its doubly coordinated neighbors or in free tertiary amides. (In addition, attempts to use spectroscopic methods to probe the unusual bonding of the amides were unsuccessful. In IR spectra, for example, carbonyl bands characteristic of the bound amides could not be distinguished from those of the trifluoroacetate ligands.) Nevertheless, the existence of a quadruply coordinated adduct provides a dramatic illustration of the ability of the oxygen atom of carbonyl compounds to accommodate multiple sites of Lewis acidity when they are linked together to form multidentate units that are structurally and electronically complementary.

4. Quadruple coordination of amides by tetradentate Lewis acids derived from 1,2-phenylenedimercury

The interaction of amides with bidentate dichloride **15** and bis(trifluoroacetate) **18** produces novel complexes in which the guests are bound in the manner of doubly coordinated bimolecular adduct **19** and quadruply coordinated termolecular adduct **21**. In principle, the two independent bidentate Lewis acids that are present in adduct **21** could be linked together to create a single macrocyclic tetradentate Lewis acid able to bind amides in the unprecedented manner of structure **22**. We have recently found that a complex of this type can be made by treating oligomeric oxide **23** [1c] with an equimolar amount of trifluoromethanesulfonic acid in ether, followed by crystallizing the product from diethylformamide [1a]. This procedure gave a 55%



23 ($R = CH_3$)



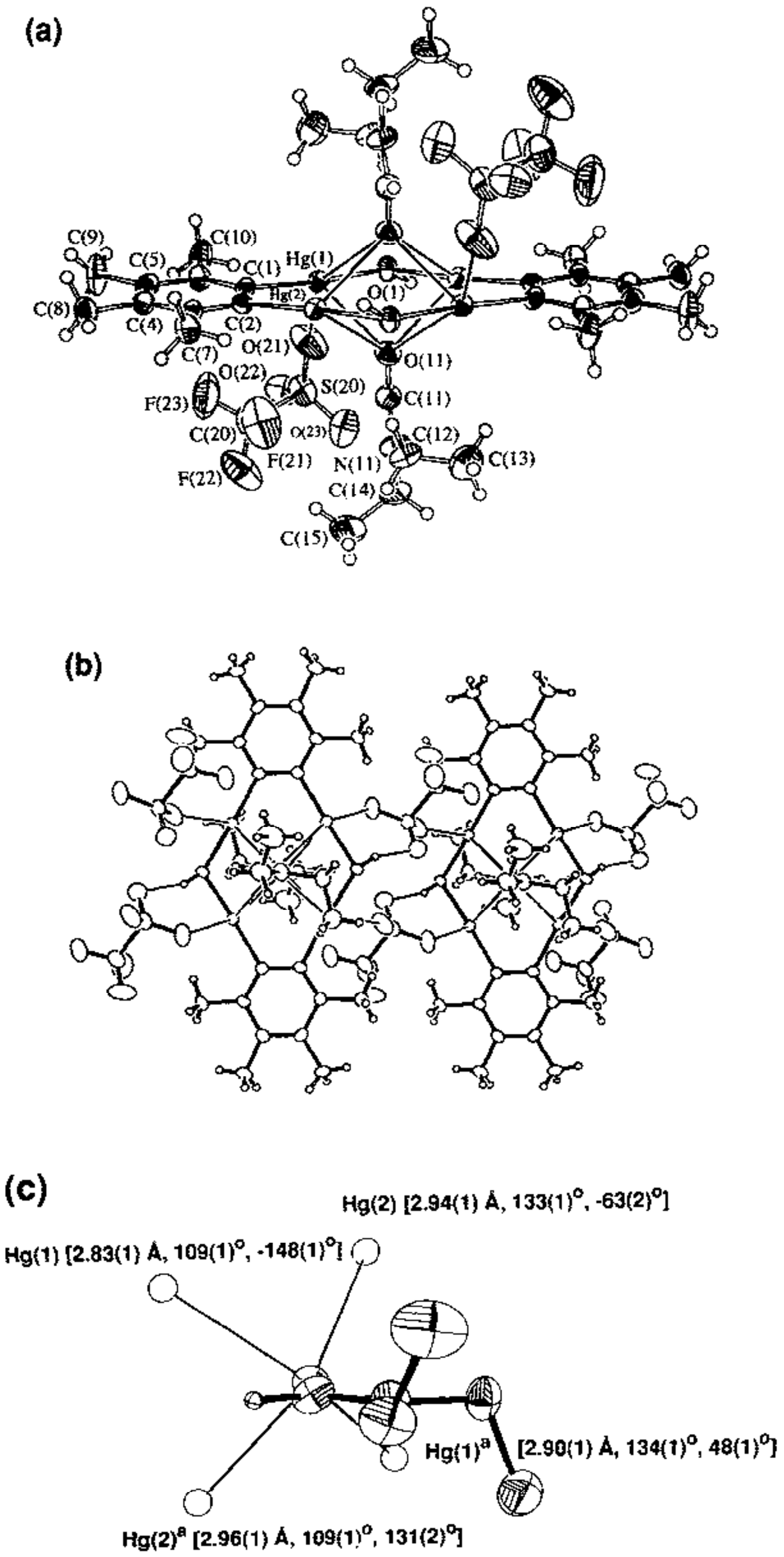
24 ($R = CH_3$)

yield of a 2:1 complex of diethylformamide with the trifluoromethanesulfonate salt **24** of a macrocyclic organomercury μ-hydroxide. The structure of the complex was determined by X-ray crystallography and is shown in Fig. 4, along with selected bond lengths and angles.

One notable feature of this structure is the presence of four Lewis acidic atoms of mercury in an approximately planar and symmetric 10-membered ring. A second remarkable feature is the binding of the two guest molecules of diethylformamide. The oxygen atom of each interacts simultaneously and almost symmetrically with all four Lewis acidic atoms of mercury, creating the partial structure shown in Fig. 4(c). All four carbonyl O $\cdots$ Hg distances are significantly shorter than the sum of the van der Waals radii of oxygen (1.40 Å) [24] and mercury (1.73 Å) [25], and the average distance (2.91(1) Å) is similar to that measured (2.88(2) Å) for the quadruply bonded amide in the 2:3 complex of bidentate bis(trifluoroacetate) **18**. However, the four atoms of mercury that surround each carbonyl oxygen atom in the complex of oxide **24** are more symmetrically disposed, and none lies close to the carbonyl plane. Atoms of mercury in adjacent rings are bridged by trifluoromethanesulfonate, which also forms a hydrogen bond with O(1) (Fig. 4(b)). The average distance for Hg—O bonds involving the trifluoromethanesulfonate group is 2.844(10) Å. Although this distance is shorter than the sum of the van der Waals radii (3.13 Å), it is still much longer than the average Hg—O distance within the 10-membered ring (2.077(8) Å) and is similar to the average Hg—O distance involving datively bound diethylformamide (2.91(1) Å). This indicates that trifluoromethanesulfonate has an important ionic character in the complex, which we express by using structure **24** to represent the fundamental molecular unit. Related salts of $(PhHg)_2OH^+$ are known and their geometric parameters are similar to those of trifluoromethanesulfonate salt **24** [32].

The carbonyl C—O distance (1.238(13) Å) in each bound amide is longer than the generally accepted value for free tertiary amides (1.22 Å) by only one standard deviation, but the N—C(O) distance (1.305(16) Å) is shorter than the normal value (1.35 Å) by a crystallographically significant amount (about 3σ) [17,28a,28b]. This demonstrates for the first time that multiple coordination by Lewis acids can have a measurable effect on the geometry of amides, despite their normal resistance to deformation [29]. In addition, the unusual bonding causes an important shift in the

Fig. 4. ORTEP drawings of the structure of the 1:2 complex of oxide **24** with diethylformamide. (a) The atomic numbering. Hydrogen atoms appear as spheres of arbitrary size and other atoms are represented by ellipsoids corresponding to 50% probability. Important bond lengths include the following: Hg(1)—C(1) = 2.053(10); Hg(2)—C(2) = 2.055(10); Hg(1)—O(1) = 2.076(8); Hg(2)—O(1)^{a} = 2.078(7); Hg(1)—O(21) = 2.806(10); Hg(2)—O(22)^{b} = 2.882(10); O(11)—C(11) = 1.238(13); N(11)—C(11) = 1.305(16) (all in ångströms). Important angles include the following: C(1)—Hg(1)—O(1) = 175.6(3)°; C(2)—Hg(2)—O(1)^{a} = 176.6(3)°; Hg(1)—O(1)—Hg(2)^{a} = 116.5(3)°. (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 and other hydrogen atoms are omitted for simplicity. The three geometric parameters that appear next to each mercury atom correspond to the average carbonyl O $\cdots$ Hg distances (Å), the C=O $\cdots$ Hg angles (degrees) and the N—C=O $\cdots$ Hg dihedral angles (degrees) for the two bound amides.


(a)
C(9)
C(10)
C(5)
C(1)
Hg(1)
Hg(2)
O(1)
C(8)
C(4)
C(2)
C(7)
O(21)
O(11)
O(22)
S(20)
C(11)
F(23)
C(20)
O(23)
C(12)
F(21)
N(11)
C(13)
F(22)
C(14)
C(15)
(b)
(c)
Hg(2) [2.94(1) Å, 133(1)°, -63(2)°]
Hg(1) [2.83(1) Å, 109(1)°, -148(1)°]
Hg(1)a [2.90(1) Å, 134(1)°, 48(1)°]
Hg(2)a [2.96(1) Å, 109(1)°, 131(2)°]

carbonyl stretching frequency, which moves from 1689 cm^{-1} (Nujol) in free diethylformamide to 1648 cm^{-1} (Nujol) in the complex with μ-hydroxide **24**. These structural and spectroscopic changes are important, because they suggest that multidentate binding may lead to enhanced reactivity of the guest.

We were unable to synthesize derivatives of bis(trifluoromethanesulfonate) **25** by treating oxide **23** with two molar equivalents of trifluoromethanesulfonic acid, so we used an alternative approach starting from dichloride **26**, which was prepared in a 73% yield by the reaction of bis(trifluoroacetate) **18** with HCl. The treatment of dichloride **26** with two equivalents of $AgOSO_2CF_3$, followed by crystallization of the product from diethylformamide, gave a 90% yield of a 1:2 complex of bis(trifluoromethanesulfonate) **25** with diethylformamide. The structure of the complex was determined by X-ray crystallography and is shown in Fig. 5, along with selected bond lengths and angles.

The complex is 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, which are relegated to secondary bridging positions in an approximately perpendicular plane. Therefore, binding of the amides is monodentate but still unusually strong, and the carbonyl C—O distance (1.25(2) Å) and N—C(O) distance (1.29(2) Å) are different from those in free amides [17,28a,28b].

This part of our work is noteworthy, because it has provided the first structural characterizations of organomercuric trifluoromethanesulfonates. (Organomercuric

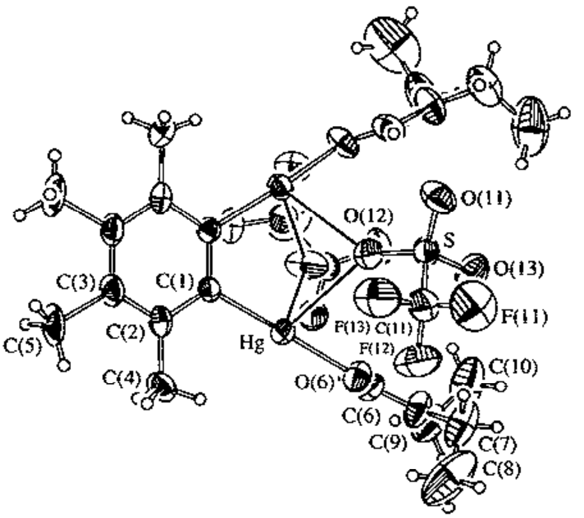


Fig. 5. ORTEP drawing of the structure of the 1:2 complex of phenylenedimercury bis(trifluoromethanesulfonate) **25** with diethylformamide. Hydrogen atoms appear as spheres of arbitrary size, and other atoms are represented by ellipsoids corresponding to 40% probability. Important bond lengths include the following: Hg—C(1) = 2.060(10); Hg O(6) = 2.065(10); Hg—O(12) = 2.884(13); O(6) C(6) = 1.25(2); N(6) C(6) = 1.29(2) (all in ångströms). Important angles include the following: O(6) Hg C(1) = 172.5(4)°.

trifluoromethanesulfonates are rarely used in chemistry and remain poorly characterized [33], despite the rapidly growing interest in trifluoromethanesulfonates of other metals [34].) In addition, it shows that it is possible to construct multidentate Lewis acids that are able to hold four electrophilic sites in an orientation that favors their simultaneous interaction with a single basic atom in a guest molecule, and it demonstrates that amides bound in this manner experience important structural and spectroscopic changes associated with enhanced reactivity.

5. Conclusions

Multidentate Lewis acids derived from 1,2-phenylenedimercury are structurally well defined and easy to make, so we considered them to be attractive candidates for exploratory studies of multiple coordination and electrophilic activation. However, their Lewis acidity is intrinsically weak and soft, so they are not ideal for the multiple coordination of bases that are weak and hard, including ketones, aldehydes and other guests of substantial practical importance in organic chemistry. For this reason, we do not expect Lewis acids derived from 1,2-phenylenedimercury to serve as genuinely useful reagents. Furthermore, the solubility of simple derivatives of 1,2-phenylenedimercury is low, so we have not yet been able to obtain valuable information about the stoichiometry, thermodynamics and kinetics of multiple coordination in solution, and also have not been able to measure the rates of reactions to establish directly that multiply coordinated carbonyl compounds experience multiple electrophilic activation. (Studies of this type are in progress, using substituted derivatives of 1,2-phenylenedimercury with much higher solubilities [35].) As a result, our study of the multiple coordination of carbonyl compounds by multidentate Lewis acids is not yet complete. However, our initial results provide very encouraging evidence that effective multidentate Lewis acids can eventually be devised for the multiple coordination and electrophilic activation of carbonyl compounds and other basic guests. In the future, such reagents may provide the organic chemist with useful new tools.

Acknowledgments

We are grateful to the Natural Sciences and Engineering Research Council of Canada, the Ministère de l'Éducation du Québec, the Canada Council and Merck Frosst for financial support. In addition, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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