

# Nanoelectrospray MS and MS–MS investigation of two polydentate Lewis acids, $(C_6F_4Hg)_3$ and $o-C_6F_4(HgCl)_2$ , characterization and halide binding selectivity

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## Abstract

The coordination of halide anions by two polyfunctional Lewis acids, namely trimeric perfluoro-*ortho*-phenylene mercury (**1**) and 1,2-bis(chloromercurio)tetrafluorobenzene (**2**) has been monitored by negative ion nanoelectrospray mass spectrometry using a hybrid quadrupole time-of-flight instrument. Experiments carried out on compound **1** in the presence of halide anions show the formation of the anionic complexes,  $[1\cdot X]^-$  and  $[(1)_2\cdot X]^-$ . The latter are likely to exhibit a bridged structure in which the halide anion is sandwiched by two molecules of **1**. In order to determine the anion binding selectivity of **1**, relative affinity measurements were carried out and reveal the following order:  $I^- > Br^- > Cl^- > F^-$ . After normalization of the halide binding affinities to that of iodide, the following values could be obtained:  $I^-$  100%,  $Br^-$   $9.5 \pm 1.6\%$ ,  $Cl^-$   $2.4 \pm 1.5\%$ , and  $F^-$   $0.3 \pm 0.1\%$  indicating that **1** is  $\sim 10\times$  less likely to bind bromide,  $\sim 40\times$  less likely to bind chloride, and  $\sim 400\times$  less likely to bind fluoride than iodide. Two fragmentation methods, namely nozzle-skimmer fragmentation and CID MS–MS, were used to further characterize the anionic complexes of **1**. Experiments carried out on **2** in the presence of different halides gave widely varied results. With excess chloride, the anionic complex  $[2\cdot Cl]^-$  is formed. In the presence of excess bromide, **2** is converted into 1,2-bis(bromomercurio)tetrafluorobenzene (**3**) and detected as the bromide complex  $[3\cdot Br]^-$ . With excess iodide, **2** undergoes a condensation reaction to form **1**, which is detected as the iodide complex  $[1\cdot I]^-$ .  
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## 1. Introduction

Motivated by the search for selective anion receptors, the coordination chemistry of anions by polydentate Lewis acids has become an area of active

research [1–4]. While several Lewis acidic main group elements have been considered at the binding site of these derivatives [5–12], the chemistry of macrocyclic polyfunctional Lewis acids containing mercury is especially well developed [13–30]. As shown by numerous studies, such compounds exhibit an unusual affinity for halide anions. Structural analysis of the resulting complexes reveal that the anion is simultaneously coordinated to three, four, five, and

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multidecker structures with hypercoordinated anions [25–31], we have demonstrated that **2** acts as a bidentate receptor toward various Lewis basic organic substrates [32–35]. In this paper, we report an electrospray mass spectrometry (ESI MS) study carried on solutions of **1** and **2** in the presence of halide anions. By analogy with a number of positive ion ESI MS studies on the host–guest chemistry of crown ethers [36–44], negative ion ESI MS [45,46] was chosen to probe the binding of inorganic ions with compounds **1** and **2**. Furthermore, based on the toxic nature of the analytes, nanoESI MS [47] was selected because detailed studies can be performed with only a few picomoles of material. In previous studies dealing with cation complexation, relative binding selectivities have been determined by comparison of the ion signals observed in mixtures of the host with different guest ions [43]. In a similar manner, we report relative halide binding selectivity for compound **1**.

## 2. Materials and methods

Compounds **1** [48] and **2** [49] were prepared according to the previously reported procedures. Purified solids were dissolved in HPLC grade acetonitrile (EM Science) at concentrations ranging from 1 to 25 pmol/ $\mu$ L. All other chemicals were obtained from Aldrich (Milwaukee, WI) or Sigma (St. Louis, MO). The stock solutions of **1** and **2** were mixed with varying concentrations of aqueous ammonium salts,  $\text{NH}_4\text{X}$ , where X is F, Cl, Br, and I. To examine the selectivity of **1**, four solutions were mixed in 50% acetonitrile, 50% deionized water, and nanoelectrosprayed: (a) 25 pmol/ $\mu$ L **1** was mixed with 6.25 pmol/ $\mu$ L of each halide, (b) 10 pmol/ $\mu$ L **1** with 10 pmol/ $\mu$ L each halide, (c) 6 pmol/ $\mu$ L **1** with 11 pmol/ $\mu$ L each halide, and (d) 2 pmol/ $\mu$ L **1** with 12 pmol/ $\mu$ L each halide.

Negative ion mass spectra were acquired using an MDS Sciex API QStar Pulsar [50] (Concord, Ont., Canada) fitted with a Protana (Odense, Denmark) nanospray ion source. Data were acquired and analyzed with TofMA 2.0RC software. The ionspray volt-

age was optimized at approximately  $-1250$  V, and no gas backpressure was used to aid nebulization. Unless specified, all spectra were obtained using a 5 V nozzle-skimmer potential to avoid skimmer region CID. Peaks were identified on the basis of their mass-to-charge ratios as well as by comparisons of their measured and theoretical isotopic distributions. The theoretical isotope profiles were calculated using Isopro 3.0 (M. Senko, available at <http://members.aol.com/msmsoft>).

To produce fragment ions, two methods were used. For “in source” nozzle-skimmer fragmentation, the potential on the nozzle was decreased from  $-35$  to  $-180$  V, as all other parameters were held constant (skimmer at  $-30$  V). For MS–MS, the voltage across the collision cell was decreased by 50–100 V, to increase the amount of internal energy imparted by collisions with  $\text{N}_2$  target gas.

## 3. Results

In the presence of fluoride, chloride, bromide, and iodide, the nanoelectrospray mass spectra of **1** contain a strong ion signal corresponding to  $[\mathbf{1}\cdot\text{X}]^-$  (X: halide anion) at  $m/z$  1068.9,  $m/z$  1084.9,  $m/z$  1128.8, and  $m/z$  1176.8, respectively (see Fig. 2). Additional species corresponding to  $[(\mathbf{1})_2\cdot\text{X}]^-$  are also observed for fluoride, chloride, bromide, and iodide at  $m/z$  2118.8,  $m/z$  2134.8,  $m/z$  2178.7, and  $m/z$  2226.7, respectively. The  $[\mathbf{1}\cdot\text{X}]^-$  species most likely corresponds to a complex in which the halide is coordinated to the three mercury centers of **1** (see Fig. 1). The  $[(\mathbf{1})_2\cdot\text{X}]^-$  ions are assigned a sandwich structure (Fig. 1) analogous to that of complexes involving mercuracarborands receptors as recently reported by Hawthorne and coworkers [17,51].

For further characterization, CID MS–MS was performed on the ion signals assigned to  $[\mathbf{1}\cdot\text{X}]^-$  and  $[(\mathbf{1})_2\cdot\text{X}]^-$ ; the results for fluoride complexes are shown in Fig. 3. In the top MS–MS spectrum, no daughter ion peaks other than the fluoride anion are observed from the fragmentation of  $[\mathbf{1}\cdot\text{F}]^-$ . In MS–MS spectra of the ion observed at  $m/z$  2118.8, assigned to the bridged complex  $[(\mathbf{1})_2\cdot\text{F}]^-$ , the only

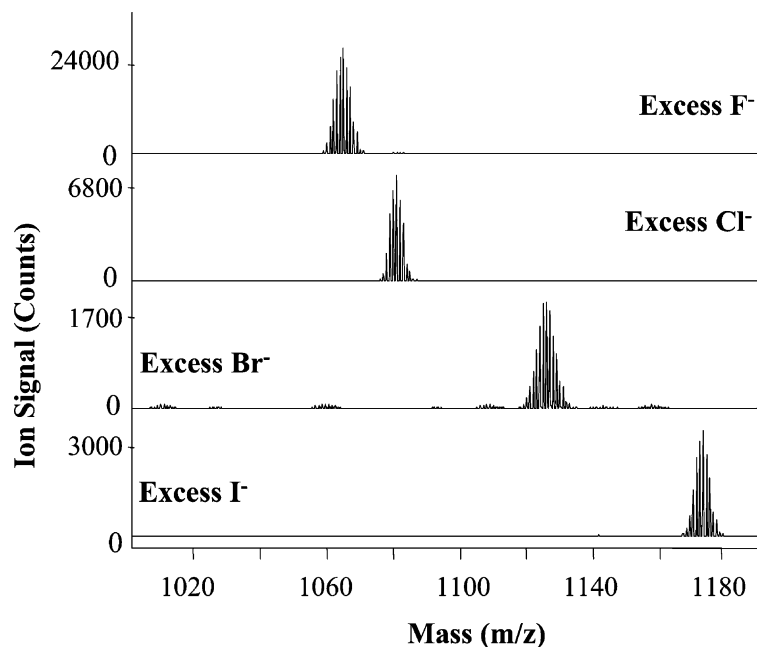


Fig. 2. Negative ion mode ESI spectra of **1** in the presence of fluoride, chloride, bromide, and iodide. The dominant ion signal corresponds to  $[\mathbf{1}\cdot\text{X}]^-$ , where X indicates the halide anion.

product ion observed at  $m/z$  1068.9, can be assigned to  $[\mathbf{1}\cdot\text{F}]^-$ . Similar results are obtained by MS–MS of complexes with the heavier halides (data not shown). The observation of the halide anion as the only frag-

ment of  $[\mathbf{1}\cdot\text{X}]^-$  is consistent with the loss of an intact neutral molecule of **1**. The dissociation of  $[(\mathbf{1})_2\cdot\text{X}]^-$  ions into the  $[\mathbf{1}\cdot\text{X}]^-$  ion signal observed in MS–MS and a neutral molecule of **1** is consistent with the

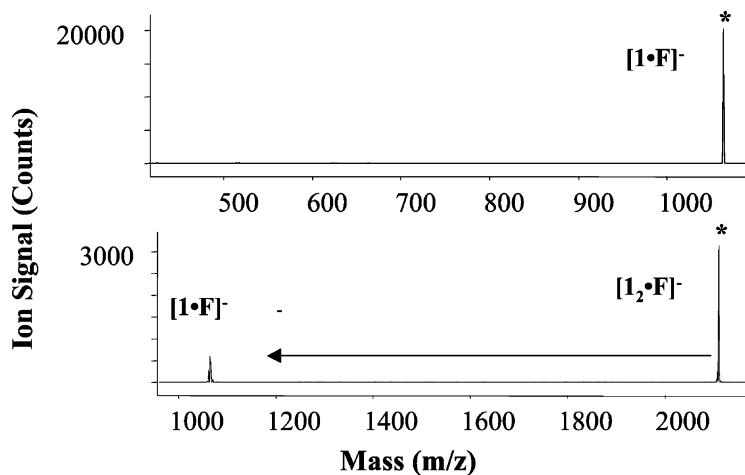


Fig. 3. MS–MS spectra of the fluoride complex of trimeric perfluoro-*ortho*-phenylene mercury  $[\mathbf{1}\cdot\text{F}]^-$  at  $m/z$  1068.9 (top), and the bridged fluoride complex with two trimeric perfluoro-*ortho*-phenylene mercury  $[(\mathbf{1})_2\cdot\text{F}]^-$  observed at  $m/z$  2118.8 (bottom). The asterisk indicates the ion signal that was selected for MS–MS.

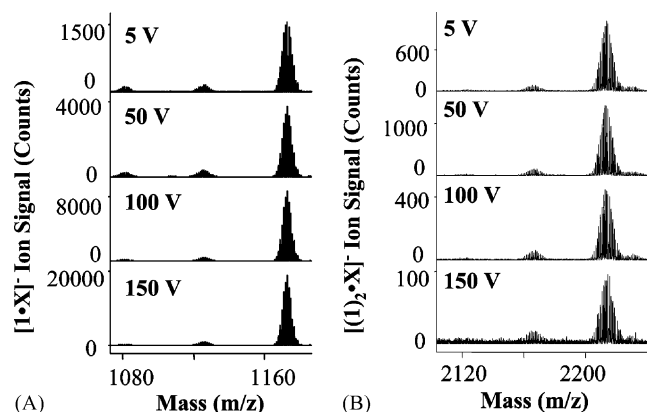


Fig. 4. Effects of in source fragmentation on  $[1\cdot X]^-$  (A) and  $[(1)_2\cdot X]^-$  (B) ion signals. Zoomed regions of the ESI mass spectra of the mixture of **1** with chloride, bromide, and iodide are shown at four nozzle-skimmer potentials.

structural assignment of the  $[(1)_2\cdot X]^-$  ion to a sandwich complex.

To determine the relative halide affinities of **1**, nanoESI MS was used to analyze mixtures of different concentrations of **1** and the four halides, present in equimolar amounts. In all cases, the ion signals corresponding to the iodide adduct,  $[1\cdot I]^-$ , dominated those corresponding to the other halide adducts. Relative binding affinities were calculated using the peak intensities (in total counts) for each of the ion signals corresponding to  $[1\cdot X]^-$  and  $[(1)_2\cdot X]^-$ . After normalization of the halide binding affinities to that of iodide, the following values could be obtained:  $I^-$  100%,  $Br^-$   $9.5 \pm 1.6\%$ ,  $Cl^-$   $2.4 \pm 1.5\%$ , and  $F^-$   $0.3 \pm 0.1\%$  indicating that **1** is  $\sim 10\times$  less likely to bind bromide,  $\sim 40\times$  less likely to bind chloride, and  $\sim 400\times$  less likely to bind fluoride than iodide. This trend in selectivity can be accounted for by Hard-Soft Acid Base Theory [52]. Because larger halide anions are intrinsically softer Lewis bases, the mercury(II) centers, which are intrinsically soft Lewis acids, will bind larger halide anions with greater affinity.

In addition to determining halide affinity, nanoESI MS can also be used to measure the stability of halide-bridged complexes,  $[(1)_2\cdot X]^-$ , relative to those of the halide adducts,  $[1\cdot X]^-$ . Using nozzle-skimmer CID, negative ion mode spectra were obtained from

a mixture of **1** with all four halides; zoomed regions are shown in Fig. 4A and B. The nozzle-skimmer potential ( $\Delta V_{NS}$ ) was varied in 25 V increments from  $-5$  to  $-150$  V. The peak intensity in counts for the halide-bridged complex,  $[(1)_2\cdot X]^-$  (Fig. 4B), was divided by the intensity of the ion signal observed for the adduct,  $[1\cdot X]^-$  (Fig. 4A). The results of these normalizations for chloride, bromide, and iodide are shown in Fig. 5. The ion signals corresponding to fluoride binding were insufficient to generate useful data. As the magnitude of the nozzle-skimmer potential increases, the dissociation of the bridged complex to form the corresponding  $[1\cdot X]^-$  ion signal increases; however, ion signals are still observed for  $[(1)_2\cdot Br]^-$  and  $[(1)_2\cdot I]^-$  at  $\Delta V_{NS} = 150$  V and for  $[(1)_2\cdot Cl]^-$  until  $\Delta V_{NS} = 125$  V (Fig. 4A). The persistence of these ion signals with increased energy input in the nozzle-skimmer region further indicates the stability of halide complexes with **1**.

In order to determine if **2** behaves as a selective bidentate Lewis acid for halide anions, a series of experiments were carried out on solutions of **2** containing chloride, bromide, and iodide. In the presence of chloride, the dominant peak in the nanoelectrospray mass spectra is observed at  $m/z$  656.8 and is assigned as  $[2\cdot Cl]^-$  (Fig. 6). The 1:1 ratio of **2** to  $Cl^-$  indicates that this species most likely exists as a chelate complex in which the chloride ion bridges both mercury

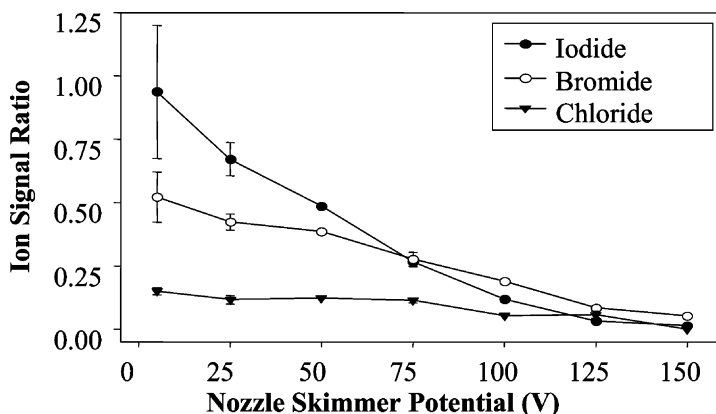


Fig. 5. Plots of the ion signals for the bridged halide complexes  $[(1)_2 \cdot X]^-$  normalized to  $[1 \cdot X]^-$  for iodide (closed circles), bromide (open circles), and chloride (black triangles) at nozzle-skimmer potentials from  $-5$  to  $-150$  V.

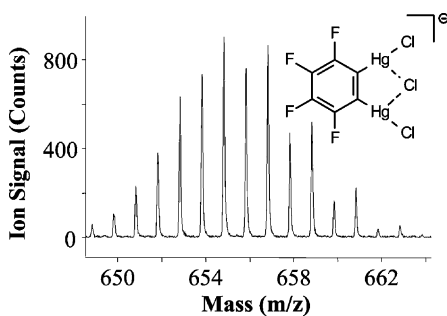


Fig. 6. Negative ion ESI mass spectrum of the chloride chelate complex of 1,2-bis(chloromercurio)tetrafluorobenzene,  $[2 \cdot Cl]^-$ .

centers. A similar chloride complex has been observed to form in solutions containing  $o$ - $C_6H_4(HgCl)_2$  and chloride anions [53]. In the presence of bromide, the dominant ion signal is observed at  $m/z$  788.7. The composition is assigned as  $[C_6F_4Hg_2Br_3]^-$ , which likely corresponds to a bromide chelate complex of 1,2-bis(bromomercurio)tetrafluorobenzene ( $[3 \cdot Br]^-$ ). In the presence of excess iodide, an ion signal corresponding to  $[1 \cdot I]^-$  is observed at  $m/z$  1176.8. This finding substantiates the occurrence of a ring closure reaction. Such reactions are not uncommon in mercury chemistry and have been previously observed upon treatment of organomercury chloride with iodide salts [54,55].

#### 4. Conclusions

The present studies show that the anionic complexes of mercury polydentate Lewis acids are amenable to analysis by ESI MS techniques. The behavior of compound **2** depends on the nature of the halide present in solution. While  $[2 \cdot Cl]^-$  is readily observed in the presence of chloride, the formation of  $[3 \cdot Br]^-$  and  $[1 \cdot I]^-$  in the presence of bromide and iodide, respectively, reflects the chemical lability of this bidentate Lewis acid. Compound **1**, however, forms anionic complexes of general formulae  $[1 \cdot X]^-$  and  $[(1)_2 \cdot X]^-$  with fluoride, chloride, bromide, and iodide. Competition studies monitored by nanoESI MS demonstrate that **1** exhibits a marked affinity for the softer halide anions. Whereas many halides complexes of polydentate mercury Lewis acids have been characterized, anion binding selectivity studies have not been reported. In that regard, the present study is especially noteworthy and indicate that the stability of the halide complex of **1** decreases in the order  $I^- > Br^- > Cl^- > F^-$ .

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