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Simultaneous coordination of dimethyl crotonthioamide by 1,8-naphthalenediylbis(mercuric trifluoroacetate)

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Abstract

Simultaneous coordination of thioamide by mercuric bidentate Lewis acids were investigated. In stoichiometric amounts of 1,8-naphthalenediylbis(mercuric trifluoroacetate) and dimethyl crotonthioamide simultaneous coordination of the two mercury sites to a single thioamide occurs. This complex is stable to small amounts of water. © 2000 Elsevier Science Ltd. All rights reserved.

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The ability of electron-deficient main group and transition metals to serve as electron acceptors and thus Lewis acids has been known for quite some time.¹ Some of the most vigorous research to date has focused on the development of chiral Lewis acids which have the ability to catalyze reactions chemoselectively and with high enantiospecificity.^{2,3} Conformational complexities are known to attend the use of monodentate Lewis acids because the Lewis acids can complex to either of the two non-bonding lone pair electrons on the carbonyl oxygen atom.⁴ The orientation of the complexation is known to have distinctly different effects on the substrate reactivity as a result of the different chemical environments created. Conformational rotomers further complicate the situation. A potential method to minimize fluxionality of complexes in solution and to organize the substrate is through the use of bidentate rather than monodentate Lewis acids. While the interaction of monodentate Lewis acids with carbonyl groups has been the focus of intensive study,^{3,4} the behavior of bidentate Lewis acids in the presence of carbonyl compounds⁵ has not been well studied. Their behavior in the presence of the thiocarbonyl group even less so.⁶ Each metal center has the opportunity to interact independently or cooperatively with a Lewis base. Of particular interest is the question of whether or not both metal centers of a bidentate Lewis acid can interact simultaneously and cooperatively to the thiocarbonyl group. Simultaneous coordination of a thiocarbonyl-containing substrate by a bidentate Lewis acid complex offers the potential for organizational control as well as double activation of the substrate (structure **1**, Fig. 1).

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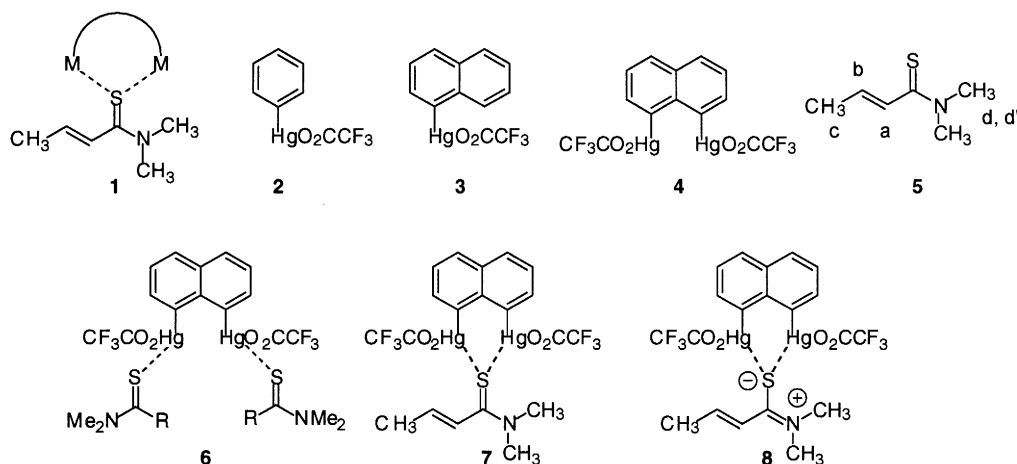


Fig. 1. Structures 1–8

Several bidentate Lewis acids containing mercury as the metal center are known and have been synthesized.⁷ Mercury Lewis acids are attractive to initiate the investigations of bidentate Lewis acids due to easy manipulation and stability. The easy exchange of ligand allows the strength of the Lewis acid to be tailored to a particular application. For our study, we chose a bidentate mercury Lewis acid with a naphthalene backbone based on several characteristics. First, the mercury atoms remain in the plane of the aromatic framework, or deviate only slightly from planarity as a result of the *peri* effect found in 1,8-disubstituted naphthalene systems.⁸ The relative planarity of the metal centers may be important for the bidentate coordination. This is due to the fact that both lone pairs of electrons on the sp^2 -hybridized sulfur atom of a thiocarbonyl group also lie in the same plane. Second, the distance between the mercury centers is suited to the formation of a bidentate chelate with a single thiocarbonyl sulfur atom. Our choice of thiocarbonyl substrate was the dimethyl crotonthioamide (**5**).

The phenylmercuric trifluoroacetate **2** and the 1,8-naphthalenediylbis(mercuric trifluoroacetate) **4** were synthesized from the known analogous mercuric chloride compounds.^{9,10} The 1-naphthalenemercuric trifluoroacetate **3** was generated from 1-bromonaphthalene: (1) (i) *n*-BuLi; (ii) HgCl_2 ; and (2) AgO_2CCF_3 . The dimethyl crotonthioamide was synthesized from the corresponding amide with Lawesson's reagent.¹¹

The main focus of our investigations is the solution structures; hence we begin with ^1H NMR studies. In the presence of 2 equivalents of thioamide **5** to the phenylmercuric trifluoroacetate, the most affected hydrogens H_a and H_b shifts from 6.54 to 6.67 and 6.98 to 7.09 ppm, respectively (Table 1, entries 1 and 2). In the presence of 1 or 2 equivalents of Lewis acid the shift is greater and maximized (6.54 to 6.79 ppm and 6.98 to 7.20 ppm, entries 3 and 4). This indicates that when the thioamide is in less than 1 equivalent, the average of the coordinated and free thioamide is shown. With 1 equivalent of 1-naphthylmercuric trifluoroacetate **3** (entry 5), the chemical shift matches the shift of the phenylmercuric trifluoroacetate **2** (entry 2) indicating a weaker interaction. With bidentate Lewis acid 1,8-naphthylbis(mercuric trifluoroacetate) **4** and 2 equivalents of thioamide, the shift approximates that of 1-naphthylmercuric trifluoroacetate indicating that there is a coordination of one thioamide to each mercury site (entry 6, structure **6**). In the presence of 1 or 2 equivalents of bidentate Lewis acid **4** to thioamide, there is a shift further downfield, especially for H_b (6.98 to 7.23 ppm) indicating a simultaneous coordination of both mercury sites to the thiocarbonyl group (structure **7**).

Carbon NMR substantiates the ^1H NMR data (Table 2). There is a trend in the chemical shift of the carbon of the thioamide group. The shift is upfield from the uncomplexed thiocarbonyl group, the largest shift being in the presence of the bidentate Lewis acid indicating simultaneous coordination. The

Table 1
¹H NMR chemical shifts for Lewis acid complexes of **5**

Entry	Lewis Acid	LA: 5	H _a (δ)	H _b (δ)	H _c (δ)	H _d (δ)	H _{d'} (δ)
1	None	0:1	6.54	6.98	1.92	3.54	3.34
2	2	1:2	6.67	7.09	1.97	3.64	3.44
3	2	1:1	6.79	7.20	2.01	3.74	3.53
4	2	2:1	6.79	7.20	2.01	3.74	3.53
5	3	1:1	6.64	7.08	1.94	3.64	3.43
6	4	1:2	6.71	7.13	1.83	3.72	3.50
7	4	1:1	6.73	7.23	2.01	3.74	3.53
8	4	2:1	6.73	7.24	2.03	3.75	3.55

upfield shift can be rationalized by the contribution of the resonance structure **8** where the thiocarbonyl carbon has a more thioiminium contribution relative to the uncomplexed compound (Fig. 1). This trend is consistent with the carbon NMR of the bidentate Lewis acid–ketone system.¹² The most indicative chemical shift is that of C_b. In excess thioamide to the bidentate Lewis acid, the chemical shift 145 ppm of C_b is close to the phenylmercuric trifluoroacetate group shift, indicating a monocoordination **6** (entry 3). However, with a 1:1 ratio, the chemical shift is 149.0 ppm indicating a simultaneous coordination **7** (entry 4).

Table 2
¹³C NMR chemical shifts for Lewis acid complexes of **5**

Entry	Lewis Acid	LA: 5	C _a (δ)	C _b (δ)	C=S(δ)
1	None	0:1	129.4	142.4	196.0
2	2	1:1	130.9	146.5	191.9
3	4	1:2	130	145	-
4	4	1:1	129.9	149.0	191.6

We have found that for the FTIR investigations following the carbonyl absorption of the trifluoroacetate group confirm the NMR investigations (Table 3). There is a distinctive shift from 1693.9 cm⁻¹ for the phenyl mercuric trifluoroacetate group to 1660.2 cm⁻¹. For the bidentate acid **4**, whether there is 1 or 2 equivalents of thioamide there is a shift from 1693.2 to 1659.9 and 1659.7 cm⁻¹ indicating that both mercury functional groups are coordinated in the presence of 1 or 2 equivalents of the thioamide (entries 4 and 5). The coordination of both mercury sites in the presence of 1 equivalent of thioamide indicates a simultaneous coordination of both mercury sites to the thiocarbonyl base as in complex **7**.

Our previous work with bidentate boron Lewis acids shows that water can be detrimental to our studies.¹² In the case of mercury, the Lewis acid should be more stable to water. Evidence for this was obtained by titrating bidentate complex **7** with water and observing the NMR spectra. Up to 3 equivalents of water were added with no indication of the complex degrading (Fig. 2b and c).

In summary, these results show that in stoichiometric amounts of bidentate Lewis acid **4** and thioamide **5**, simultaneous coordination occurs in solution. In the presence of excess thioamide, each of the Lewis

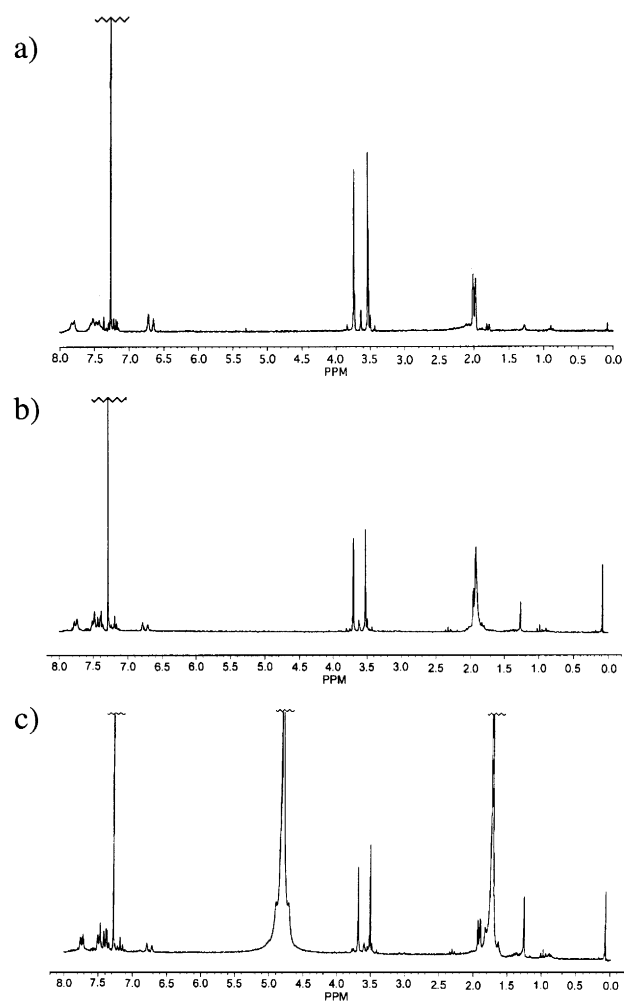


Fig. 2. ^1H NMR spectra of: (a) complex **7**; (b) complex **7**+1 equiv. of H_2O ; (c) complex **7**+3 equiv. of H_2O

Table 3
FTIR stretches of the trifluoroacetate carbonyl groups for Lewis acid complexes of **5**

Entry	Lewis Acid	LA: 5	C=O (cm^{-1})
1	2	1:0	1693.9
2	2	1:1	1660.2
3	4	1:0	1693.2
4	4	1:2	1659.9
5	4	1:1	1659.7

acidic mercury coordinates with a thioamide **5**. Very importantly, small amounts of water do not affect this bidentate coordination.

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