

(Mn<sub>1-x</sub>Mo<sub>x</sub>)<sub>3</sub>B<sub>4</sub> the *c* axis changes from 0.295 to 0.305 nm, and it is expected that the nearest Mn-Mn distance crosses the maximum point of the exchange energy and the Curie temperature shows the indicated cuplike variation. It seems that the relation between magnetic interaction and nearest Mn-Mn distance is quite similar to that of NiAs type intermetallic compounds.

Registry No. Mn<sub>3</sub>B<sub>4</sub>, 12229-02-6; Cr<sub>3</sub>B<sub>4</sub>, 12045-71-5; Mo<sub>3</sub>B<sub>4</sub>, 12310-46-2.

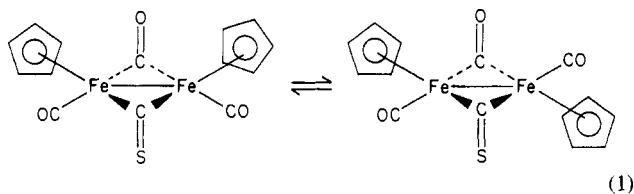
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### Lewis Acid Adducts of the Bridging Thiocarbonyl in ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS)

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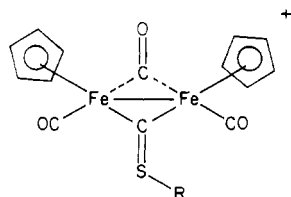
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We recently described the synthesis of the thiocarbonyl-bridged Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS) dimer (Cp =  $\eta$ -C<sub>5</sub>H<sub>5</sub>).<sup>2,3</sup> Like the ruthenium analogue,<sup>4</sup> Cp<sub>2</sub>Ru<sub>2</sub>(CO)<sub>3</sub>(CS), the iron dimer exists in solution as an equilibrium mixture of the *cis* and *trans* isomers:



An X-ray diffraction study has established the structure of the *cis* isomer in the solid state.<sup>5</sup>

The reactivity of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS) has a certain similarity to that of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub>. It reacts with phosphines, phosphites, and CNMe to give the substituted Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(L)(CS) products.<sup>6</sup> It is cleaved by Na amalgam, yielding CpFe(CO)(CS)<sup>-</sup> and CpFe(CO)<sub>2</sub><sup>-2</sup>. On the other hand, its reactivity<sup>2</sup> with Me<sub>2</sub>S<sub>2</sub>, halogens, and O<sub>2</sub> with HBF<sub>4</sub> is quite different than is observed with Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub>. Also Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS) reacts readily with alkyl iodides and other alkylating agents to give the S-alkylated products:<sup>3,6</sup>



While no CO-alkylated products of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> have been reported, certain Lewis acids such as AlEt<sub>3</sub> do form adducts

with the bridging CO groups.<sup>7-9</sup> In the present report, we describe Lewis acid adducts of the bridging CS group in Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS). Related to this research is the report of the formation of Lewis acid adducts of the triply bridging CS in (CpCo)<sub>3</sub>(S)(CS).<sup>10</sup> Also, it is well-known that terminal CS groups in electron-rich complexes form adducts with Lewis acids and are alkylated at the CS sulfur atom.<sup>11-14</sup>

### Experimental Section

**General Procedures.** All reactions were carried out under a pre-purified N<sub>2</sub> atmosphere with use of Schlenk equipment. Unless indicated otherwise, reactions were conducted at room temperature.

Molar conductivities were measured in nitromethane solutions at 25 °C with an Industrial Instruments RC-16B2 conductivity bridge. A Perkin-Elmer 337 or 237B instrument was used to record infrared spectra; 1-mm path length NaCl cells were used for most spectra, which were calibrated with CO gas (CO region) and polystyrene (CS region); band positions are believed to be accurate to within ±2 cm<sup>-1</sup>. Proton NMR spectra were recorded on a Varian HA-100 spectrometer, with tetramethylsilane (Me<sub>4</sub>Si) as an internal reference. Elemental analyses were performed by Galbraith Laboratories.

**Solvents and Reagents.** Nitromethane for conductivity measurements was dried over P<sub>4</sub>O<sub>10</sub>, fractionally distilled twice under N<sub>2</sub>, and stored over type 4A molecular sieves under N<sub>2</sub>. All other solvents were reagent grade and were stored over 4A sieves and purged with N<sub>2</sub> before use.

The thiocarbonyl complex Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS) was prepared as previously described.<sup>2</sup> The carbonyl complexes Et<sub>4</sub>N[M(CO)<sub>5</sub>I] (M = Cr, W)<sup>15</sup> and [CpFe(CO)<sub>2</sub>(THF)]BF<sub>4</sub><sup>16</sup> were prepared by literature methods. All other reagents were of the highest purity available and were used as received.

**Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>CS·HgX<sub>2</sub> (X = Cl, Br, I).** Mercuric iodide (0.227 g, 0.500 mmol) was added to a solution of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS) (0.187 g, 0.505 mmol) in 30 mL of acetone, and the mixture was stirred for 10 min. Evaporation of the solvent under reduced pressure gave a dark red residue, which was dried in vacuo for several hours. The product was transferred to a frit filter, washed thoroughly 10 times with 20 mL of pentane, and again vacuum-dried. Yield of the product, Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>CS·HgI<sub>2</sub>, was essentially quantitative. Anal. Calcd for C<sub>14</sub>H<sub>10</sub>Fe<sub>2</sub>HgI<sub>2</sub>O<sub>3</sub>S: C, 20.40; H, 1.22. Found: C, 19.87; H, 1.34.

The adducts Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>CS·HgCl<sub>2</sub> and Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>CS·HgBr<sub>2</sub> were obtained in the same manner, except that CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent.

**[Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>CS·HgMe]PF<sub>6</sub>.** Methylmercuric chloride (0.13 g, 0.52 mmol) was dissolved in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> at 0 °C, and AgPF<sub>6</sub> (0.13 g, 0.51 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added. The mixture was stirred for 15 min and then Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS) (0.20 g, 0.54 mmol) was added, giving a dark red mixture. After 5 min the solution was filtered to remove AgCl, 30 mL of hexane was added, and the solution was evaporated; the crystals thus obtained were filtered off and washed with Et<sub>2</sub>O. Two more crystallizations in this manner gave dark red needles of [Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>CS·HgMe]PF<sub>6</sub> sufficiently pure for analysis (0.25 g, 67%). Anal. Calcd for C<sub>15</sub>H<sub>13</sub>Fe<sub>2</sub>HgO<sub>3</sub>PS: C, 24.66; H, 1.79. Found: C, 24.99; H, 1.86.

**Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>CS·M(CO)<sub>5</sub> (M = Cr, W).** A solution of Et<sub>4</sub>N[Cr(CO)<sub>5</sub>I] (0.229 g, 0.510 mmol) in 30 mL of acetone was cooled to 0 °C, and then AgBF<sub>4</sub> (0.100 g, 0.513 mmol) in 10 mL of acetone was added over 5 min from an equippressure dropping funnel. After an additional 10 min, the mixture was filtered under N<sub>2</sub> to remove AgI, and the yellow-orange filtrate was again cooled to 0 °C. The thiocarbonyl complex (0.191 g, 0.516 mmol) was added, and the

- (1) Based on the Ph.D. dissertation submitted by M.H.Q. to Iowa State University, 1978.
- (2) Quick, M. H.; Angelici, R. J. *J. Organomet. Chem.* **1978**, *160*, 231.
- (3) Wagner, R. E.; Jacobson, R. A.; Angelici, R. J.; Quick, M. H. *J. Organomet. Chem.* **1978**, *148*, C35.
- (4) Wnuk, T. A.; Angelici, R. J. *Inorg. Chem.* **1977**, *16*, 1173.
- (5) Beckman, D. E.; Jacobson, R. A. *J. Organomet. Chem.* **1979**, *179*, 187.
- (6) Quick, M. H.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 1123.

- (7) Alich, A.; Nelson, N. J.; Strobe, D.; Shriver, D. F. *Inorg. Chem.* **1972**, *11*, 2976.
- (8) Kim, N. E.; Nelson, N. J.; Shriver, D. F. *Inorg. Chim. Acta* **1973**, *7*, 393.
- (9) Shriver, D. F. *J. Organomet. Chem.* **1975**, *94*, 259.
- (10) Werner, H.; Leonhard, K.; Kolb, O.; Röttinger, E.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 1654.
- (11) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 7568.
- (12) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 1261.
- (13) Dombek, B. D.; Angelici, R. J. *Inorg. Chem.* **1976**, *15*, 2397.
- (14) Greaves, W. W.; Angelici, R. J. *J. Organomet. Chem.* **1980**, *191*, 49.
- (15) Greaves, W. W.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 4108.
- (16) Abel, E. W.; Butler, I. S.; Reid, J. G. *J. Chem. Soc.* **1963**, 2068.
- (17) Reger, D. L.; Coleman, C. J. *J. Organomet. Chem.* **1977**, *131*, 153.

Table I. Infrared and  $^1\text{H}$  NMR Data for  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$  Adducts

compd	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{CS}), \text{cm}^{-1}$	$\delta(\text{Cp})^a$	$\delta(\text{R})^a$
$\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$	2004 vs, 1968 m, 1805 m <sup>b</sup>	1124 m <sup>b</sup>	4.79, 4.85 (2:5) <sup>c,d</sup>	
$[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS}-\text{Me})]\text{PF}_6$	2040 s, 2012 w, 1856 m <sup>b</sup>	1028 w <sup>b</sup>	5.65 (br) <sup>c</sup>	3.77 (Me) <sup>c</sup>
$\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{HgCl}_2$	2037 s, 2004 m, 1842 m <sup>e</sup>	1020 w <sup>e</sup>	5.54 <sup>f</sup>	
$\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{HgBr}_2$	2035 s, 2006 m, 1840 m <sup>e</sup>	1020 w <sup>e</sup>		
$[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS}-\text{HgMe})]\text{PF}_6$	2033 s, 1998 m, 1844 s <sup>b</sup>	1017 w <sup>b</sup>	5.59 <sup>g</sup>	1.33 (Me, br) <sup>g</sup>
$\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{Cr}(\text{CO})_5$	2061 m, 2020 s, 2005 w, 1977 w, 1934 s, 1916 m, 1825 m <sup>h</sup>	1082 w <sup>h</sup>	5.28 <sup>c</sup>	
$\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{W}(\text{CO})_5$	2067 m, 2022 s, 1992 w, 1977 w, 1931 s, 1911 m, 1827 m <sup>h</sup>	1076 w <sup>h</sup>	5.28 <sup>c</sup>	
$[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}-\text{FeCp}(\text{CO})_2]\text{BF}_4$	2049 vs, 2025 s, 2006 m, 1834 m <sup>b</sup>		5.45, 5.73 <sup>g,i</sup>	

<sup>a</sup> Downfield from  $\text{Me}_4\text{Si}$ . <sup>b</sup> In  $\text{CH}_2\text{Cl}_2$  solution. <sup>c</sup> In  $\text{CDCl}_3$  solution. <sup>d</sup> Relative peak areas in parentheses.  $\delta$  4.85 is assigned to the cis isomer and  $\delta$  4.79 to the trans.<sup>2</sup> <sup>e</sup> In  $\text{CH}_2\text{Cl}_2$  saturated with  $\text{HgX}_2$ . <sup>f</sup> In  $\text{CDCl}_3$  saturated with  $\text{HgCl}_2$ . <sup>g</sup> In acetone- $d_6$  solution. <sup>h</sup> In  $\text{CS}_2$  solution. <sup>i</sup> Cp of adduct group.

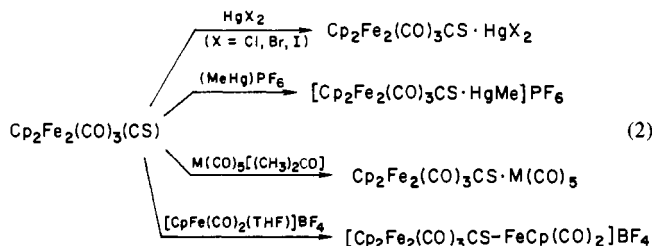
mixture was stirred for 30 min. The solution was then warmed to room temperature, and the solvent was evaporated under reduced pressure. Extraction of the residue with 4:1 pentane/acetone and filtration gave a deep red solution, which was evaporated under a slow stream of  $\text{N}_2$  to give red-purple needles of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{Cr}(\text{CO})_5$  (0.16 g, 59%). Anal. Calcd for  $\text{C}_{19}\text{H}_{10}\text{CrFe}_2\text{O}_8\text{S}$ : C, 40.60; H, 1.79. Found: C, 40.01; H, 1.94.

The same reaction with  $\text{Et}_4\text{N}[\text{W}(\text{CO})_5\text{I}]$  (0.296 g, 0.510 mmol) afforded  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{W}(\text{CO})_5$  as red-purple needles (0.27 g, 76%). Anal. Calcd for  $\text{C}_{19}\text{H}_{10}\text{Fe}_2\text{O}_8\text{SW}$ : C, 32.89; H, 1.45; S, 4.62. Found: C, 33.08; H, 1.15; S, 4.68.

$[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}-\text{CpFe}(\text{CO})_2]\text{BF}_4$ . A mixture of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$  (0.20 g, 0.54 mmol) and  $[\text{CpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$  (0.17 g, 0.50 mmol) in 35 mL of acetone was refluxed for 1 h. The solvent was removed under reduced pressure, and the residue was dried in vacuo overnight. The red product was transferred to a frit filter, washed five times with 20 mL of  $\text{Et}_2\text{O}$ , and then recrystallized from 1:1  $\text{CH}_2\text{Cl}_2$ /hexane at  $-20^\circ\text{C}$  to give red-brown crystals of the adduct (0.26 g, 82%); molar conductivity  $\Lambda = 77.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Anal. Calcd for  $\text{C}_{21}\text{H}_{15}\text{BF}_4\text{Fe}_3\text{O}_5\text{S}$ : C, 38.90; H, 2.59; S, 5.12. Found: C, 39.00; H 2.37; S, 5.12.

## Results and Discussion

The reaction of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$  with certain Lewis acids gives neutral or cationic S-adduct complexes (eq 2). Like the S-alkyl analogues,  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}-\text{R}^+$ ,<sup>6</sup> these compounds are dark red in the solid state and in solution. In the solid state they are air stable.



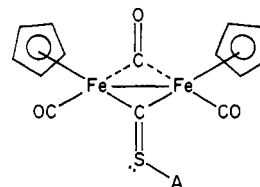
The  $\text{HgX}_2$  adducts are very labile in solution and are largely dissociated in the absence of excess mercuric halide. For this reason, IR and NMR spectra (Table I) of these compounds were measured on solutions saturated with excess  $\text{HgX}_2$ . It should be noted that  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$  reacts with  $\text{HgX}_2$  to cleave the dimer and give  $\text{CpFe}(\text{CO})_2\text{X}$  and  $\text{CpFe}(\text{CO})_2\text{HgX}$ .<sup>17</sup> Presumably the coordinating ability of the bridging CS group and the resistance of the CS-bridged Fe-Fe bond<sup>2</sup> to cleavage take the reactions of  $\text{HgX}_2$  with  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$  and  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$  on different pathways.

While  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{HgX}_2$  dissociates spontaneously in solution, the other S-adduct groups must be displaced by added ligands. For example,  $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS}-\text{HgMe})]^+$  reacts slowly with halide ions in solution to yield  $\text{MeHgX}$  and

$\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$ . The complex  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{W}(\text{CO})_5$  reacts with  $\text{I}^-$  in warm acetone to give  $\text{W}(\text{CO})_5\text{I}^-$  and  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$ . Also, ligands (L) such as  $\text{PPh}_3$  and pyridine react with the metal carbonyl adducts to give  $\text{M}(\text{CO})_5\text{L}$  or  $\text{CpFe}(\text{CO})_2\text{L}^+$  and the iron dimer. These results suggest that  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$  is a more weakly coordinating ligand than these more common ligands.

The reactions of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$  with  $\text{BX}_3$  (X = F, Cl, Br),  $\text{AlCl}_3$ ,  $\text{Fe}(\text{CO})_4(\text{THF})$ ,  $\text{Mo}(\text{CO})_5[(\text{CH}_3)_2\text{CO}]$ ,  $\text{W}(\text{CO})_5[(\text{CH}_3)_2\text{CO}]$ , and  $[\text{M}(\text{CO})_5(\text{NCMe})]\text{PF}_6$  (M = Mn, Re) gave evidence such as a red coloration or an appropriate IR spectrum of S-adduct formation, but stable products could not be isolated in these cases. We were not successful in isolating a pure product, presumably  $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})]_2\text{PtCl}_2$ , obtained from the reaction of  $\text{PtCl}_2(\text{NCPH})_2$  with the dimer. Although  $\text{Ag}^+$  gives an S adduct with the terminal CS group in  $\text{W}(\text{diphos})_2(\text{CO})(\text{CS})$ ,<sup>13</sup> the product of the reaction of  $\text{Ag}^+$  with  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$  was not an S adduct but was not otherwise characterized.

All of these Lewis acid adducts, like the S-alkyl derivatives  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS}-\text{R})^+$ ,<sup>3,6</sup> are believed to have the structure in which the Cp groups are cis to each other:



This assignment is based primarily upon the number and relative intensities of the terminal  $\nu(\text{CO})$  absorptions (Table I). In  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$  and related systems,<sup>4,6</sup> the cis isomer exhibits two terminal  $\nu(\text{CO})$  bands with the higher frequency absorption having the greater intensity. The IR spectrum of the trans isomer shows only one  $\nu(\text{CO})$  band. X-ray studies have confirmed cis structural assignments for  $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS}-\text{Et})]^+$ <sup>3</sup> and  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$ .<sup>18</sup> Although the two  $\nu(\text{CO})$  bands characteristic of a cis structure are evident in spectra of most of the complexes, they are assigned to the 2020 s and 2005 w  $\text{cm}^{-1}$  absorbances of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{Cr}(\text{CO})_5$ , the 2022 s and 1992 w  $\text{cm}^{-1}$  bands of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{W}(\text{CO})_5$ , and the 2025 s and 2006 m  $\text{cm}^{-1}$  absorbances of  $[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}-\text{FeCp}(\text{CO})_2]^+$  by analogy with the other adducts; the remaining  $\nu(\text{CO})$  bands of the metal carbonyl adducts may then be assigned to the other CO groups in the molecules. The frequencies and intensities of the remaining absorptions in the Cr and W complexes compare favorably with those in the somewhat related thioketone complexes  $(\text{Me}_2\text{C}=\text{S})\text{M}(\text{CO})_5$ , where M is Cr or W.<sup>19</sup>

(17) Thomas, J. U.S. Patent 2849 471, Aug 26, 1958; *Chem. Abstr.* 1959, 53, 4298.

(18) Dunker, J. W.; Finer, J. S.; Clardy, J.; Angelici, R. J. *J. Organomet. Chem.* 1976, 114, C49.

As expected, the effect in the IR of adding a Lewis acid to the sulfur of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$  is to increase all of the  $\nu(\text{CO})$  frequencies (Table I). The effect on the  $\nu(\text{CS})$  absorption is to shift it to lower frequency and to substantially decrease its relative intensity.

The electron-withdrawing effect of the Lewis acids may also be seen in the downfield shift of the Cp protons in the  $^1\text{H}$  NMR spectra of the adducts as compared to that of the free dimer (Table I). The nonlinear  $\text{C}=\text{S}-\text{A}$  bond should make the two Cp rings inequivalent in the  $^1\text{H}$  NMR spectra of the adducts, as observed in several *S*-alkyl derivatives.<sup>3,6,18</sup> However, in none of the adducts are the Cp rings inequivalent. In the  $\text{HgCl}_2$  adduct, it is possible that dissociation and association of  $\text{HgCl}_2$  occur sufficiently rapidly to make the Cp rings equivalent on the NMR time scale. However, for the other complexes, it seems unlikely that dissociation would be so rapid. In these cases, the Cp groups could be fortuitously equivalent or they could become equivalent on the NMR time scale by rapid rotation around the  $\text{C}=\text{S}$  bond or inversion at the sulfur atom. The reason for their equivalence is not clear from the data currently available.

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**Registry No.**  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{HgCl}_2$ , 80422-41-9;  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{HgBr}_2$ , 80422-42-0;  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{HgI}_2$ , 80422-43-1;  $[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{HgMe}]\text{PF}_6$ , 80422-37-3;  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{Cr}(\text{CO})_5$ , 80422-40-8;  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{W}(\text{CO})_5$ , 80434-41-9;  $[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}\cdot\text{CpFe}(\text{CO})_2]\text{BF}_4$ , 80422-39-5;  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$ , cis isomer, 71154-94-4;  $\text{Et}_4\text{N}[\text{Cr}(\text{CO})_5\text{I}]$ , 14780-98-4;  $\text{Et}_4\text{N}[\text{W}(\text{CO})_5\text{I}]$ , 14781-01-2;  $[\text{CpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$ , 63313-71-3;  $\text{HgCl}_2$ , 7487-94-7;  $\text{HgBr}_2$ , 7789-47-1;  $\text{HgI}_2$ , 7774-29-0;  $\text{MeHgCl}$ , 115-09-3;  $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS}\cdot\text{Me})]\text{PF}_6$ , 76189-80-5;  $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$ , trans isomer, 80446-94-2.

(19) Gingerich, R. G. W.; Angelici, R. J. *J. Organomet. Chem.* **1977**, *132*, 377. Karcher, B. A.; Jacobson, R. A. *Ibid.* **1977**, *132*, 387. Gingerich, R. G. W.; Angelici, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 5604.

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### Specific Sequestering Agents for the Actinides. 8. Synthesis and Structural Chemistry of Tetrakis(thiohydroxamato)hafnium(IV) in $\text{Hf}(\text{CH}_3\text{C}_6\text{H}_4(\text{S})\text{N}(\text{O})\text{CH}_3)_4\cdot\text{C}_2\text{H}_5\text{OH}^1$

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A continuing project in this laboratory has been the design and synthesis of specific sequestering agents for the actinide(IV) ions. The degree of success so far achieved in this goal has been reviewed recently.<sup>1-4</sup> The approach used relies on

Table I. Summary of Crystal Data for  $\text{Hf}(\text{C}_9\text{H}_{10}\text{NOS})_4\cdot\text{C}_2\text{H}_5\text{OH}$

formula weight	945.5
space group	$P\bar{1}$
cell constants <sup>a</sup>	
<i>a</i>	10.501 (1) Å
<i>b</i>	10.958 (1) Å
<i>c</i>	18.684 (2) Å
$\alpha$	97.388 (8)°
$\beta$	93.136 (8)°
$\gamma$	98.205 (9)°
cell volume	2014.4 (4) Å <sup>3</sup>
formula units/cell, <i>Z</i>	2
calcd density	1.49 g cm <sup>-3</sup>
obsd density	1.50 (1) g cm <sup>-3</sup>
cryst dimens	0.35 × 0.30 × 0.18 mm
abs coeff, $\mu(\text{Mo K}\alpha)$	28.5 cm <sup>-1</sup>

<sup>a</sup> Conditions: ambient temperature 23 °C; Mo  $\text{K}\alpha_1$  radiation;  $\lambda = 0.70926$  Å.

the similar coordination chemistry of high-spin  $\text{Fe}^{3+}$  and  $\text{Pu}^{4+}$ ,<sup>2,3,5</sup> and the molecular architecture of the siderophores (ferric ion specific chelating agents of microbial origin). While hydroxamate and catecholate chelating groups are the primary functional groups in siderophores, the thiohydroxamate chelating unit also occurs in at least one compound of natural origin.<sup>6</sup>

The tetrakis(catecholato)metalate(IV) complexes of Th(IV), U(IV), and Hf(IV) have all been prepared and structurally characterized.<sup>7,8</sup> They are isostructural, with the  $D_{2d}$  coordination symmetry of the trigonal-faced dodecahedron. Both the hydroxamate complexes tetrakis(*N*-isopropyl-3,3-dimethylbutanehydroxamato)thorium(IV)<sup>2</sup> and tetrakis(*N*-phenylbenzohydroxamato)hafnium(IV)<sup>9</sup> have this same  $D_{2d}$  geometry. In contrast, the more sterically hindered complex, tetrakis(*N*-isopropyl-2,3-dimethylpropanehydroxamato)thorium(IV), is distorted substantially toward a cubic coordination polyhedron.<sup>2</sup> No tetrakis(thiohydroxamate) complexes have been structurally characterized to date.

Determination of the coordination geometry of the unconstrained tetrakis(bidentate)metalate(IV) complexes are a fundamental component in the design of an octadentate chelating agent that incorporates four such functionalities to form an optimum metal coordination environment. While we have prepared thiohydroxamate complexes of Th(IV), no crystals suitable for structure analysis have been obtained. Instead, we report the synthesis and structural characterization of the hafnium complex, the title compound.

### Experimental Section

**Synthesis of Compounds.** Tetrakis(*N*-methyl-*p*-thiotolylhydroxamato)hafnium(IV)-Ethanol. An aqueous solution of hafnium tetrachloride (1.0 g, 3.12 mmol) in 10 mL of water was added to a stirred aqueous solution of sodium *N*-methyl-*p*-thiotolylhydroxamate (2.53 g, 12.5 mmol); the mixture was stirred for 5 min, and the white precipitate was filtered, washed with water, and dried in vacuum over  $\text{P}_2\text{O}_5$ . The compound was recrystallized from acetone-ethanol solution by slow evaporation. The crystals lose solvent easily in air. A sample for analysis was dried under high vacuum. The complexes are very hygroscopic and were partially hydrated just prior to analysis. Anal. Calcd for  $\text{Hf}(\text{C}_9\text{H}_{10}\text{NOS})_4$ : C, 48.13; H, 4.49; N, 6.23; S, 14.27. Calcd for  $\text{Hf}(\text{C}_9\text{H}_{10}\text{NOS})_4\cdot\text{H}_2\text{O}$ : C, 47.13; H, 4.61; N, 6.10; S, 14.00. Found: C, 47.43; H, 4.74; N, 6.12; S, 13.05.

- (1) Previous paper in this series: Weilt, F. L.; Raymond, K. N. *J. Org. Chem.* **1981**, *46*, 5234-37. A preliminary account of this work appeared at the 180th National Meeting of the American Chemical Society, Las Vegas, Aug 1980 (see Abstract INOR 300).
- (2) Smith, W. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 3341.
- (3) Smith, W. L.; Raymond, K. N. *Struct. Bonding (Berlin)* **1981**, *43*, 159-186. Raymond, K. N.; Smith, W. L.; Weilt, F. L.; Durbin, P. W.; Jones, E. S.; Abu-Dari, K.; Sofen, S. R.; Cooper, S. R. In "Lanthanides and Actinides"; Edelstein, N. M., Ed.; American Chemical Society: Washington, D.C., 1980; ACS Symp. Ser. No. 131, pp 143-72. Weilt, F. L.; Raymond, K. N.; Smith, W. L.; Howard, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 1170-12.

- (4) *New York Times*, Sept 13, 1980; p 8.
- (5) Weilt, F. L.; Raymond, K. N. "Abstracts of papers", 180th National Meeting of the American Chemical Society, Las Vegas, Aug 1980; American Chemical Society: Washington, D.C., 1980; INOR 109.
- (6) Raymond, K. N.; Carrano, C. J. *Acc. Chem. Res.* **1979**, *12*, 183-90.
- (7) Sofen, S. R.; Abu-Dari, K.; Freyberg, D. P.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 7882-87.
- (8) Sofen, S. R.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 1611-16.
- (9) Teanqui, D.; Laugier, J.; Boyer, P.; Vullket, P. *Acta Crystallogr.*, **1978**, *B34*, 767-73.