X-Ray Crystal Structures of Metal Thiolates

John Tidwell, Chelsea Iluno| Clinton D. Bryan, Danny G. McGuire| Cameron University, Lawton, Ok, 73505, United States

Abstract

Metal thiolates have been an important factor in regulating electron transport, but are yet to be fully understood. The X-ray structural characterization of metal thiolates, such as a revisit of $[CpFe(CO)(\mu^2\text{-}SC_6H_4OCH_3)]_2$ which we reported earlier, will begin to provide a better idea of the internal chemistry of such compounds. X-ray data for this report were collected using an Enraf-Nonius CAD4 diffractometer.

Background

Organisms at all levels of complexity have been found to have iron-sulfur proteins. Many of these proteins have interactions with two iron atoms through cysteine side chains. These iron-sulfur structures at active sites are involved in electron transport as well as a number of other catalytic functions. Electron-tunneling calculations indicate an efficient electron-transfer pathway from the [Fe2S2] cluster to a heme.[1] Using phenyl thiolates as the ligands complexing the iron atoms, the substitution of the phenyl ring can affect the electron donating power of the thiolate sulfur which should affect the covalency of the metal-ligand bond.[2] To probe the inductive effect, it is necessary to evaluate substituents which have varying electron-withdrawing and –donating strengths. McGuire et al. found that the carbonyl frequency might be employed as a gauge of the donor ability of the thiolate ligand.[3] They also reported that reduction of Fe-S distances, as determined by single-crystal X-ray crystallography, was indicative of diminished $Fe_{d\pi}\text{-}S_{p\pi}$ antibonding.[3]

Methods

General Method for X-ray Crystallography

crystal mount	on glass fiber by epoxy
cell detn, refls	25
cell detn, 2θ range, deg	10-26
radiation	MoKα, graphite monochromated
γ,Å	0.71073
temp, K	293
Diffractometer	Enraf-Nonius CAD-4 at Cameron University
scan technique	θ-2θ
scan speed, deg min^{-1}	4-16 (in omega)
scan width, deg	1.0 +0.35 tan θ
2θ range, deg	2-50
absorption correction	Empirical psi scans
solution method	Direct method
extinction	None
programs	WinGX,[4] SHELX,[5] ORTEP3,[4]
scattering factors	International Tables for Crystallography Vol. 4
H atom treatment	Hydrogen atoms idealized and refined with riding constraints

Formula	$[CpFe(CO)(SC_6H_4OCH_3)]_2$ (1)	$[CpFe(CO)(SC_6H_4CF_3)]_2$ (2)
crystal size, mm	0.23 x 0.16 x 0.06	0.52 x 0.19 x 0.06
crystal color	Red	Colorless
a,b,c, Å	20.720 (8), 12.471 (5), 21.122 (7)	10.491(4), 12.305(5), 12.794(4)
α,β,γ deg	90, 114.94 (3), 90	61.26(3), 67.42(4), 68.428(3)
space group	C 2/c	P -1
Z	8	2
F (000)	2367.65	655.91
Refl meas, unique, obsd	8698, 3744, 1746	4853, 4573, 2865
R for merge	0.081	0.0286
parameters refined	307	343
$R(_F{}^2), R_W(_F{}^2)$	0.082,0.176	0.0691, 0.161
GOF	0.989	1.064

Structures
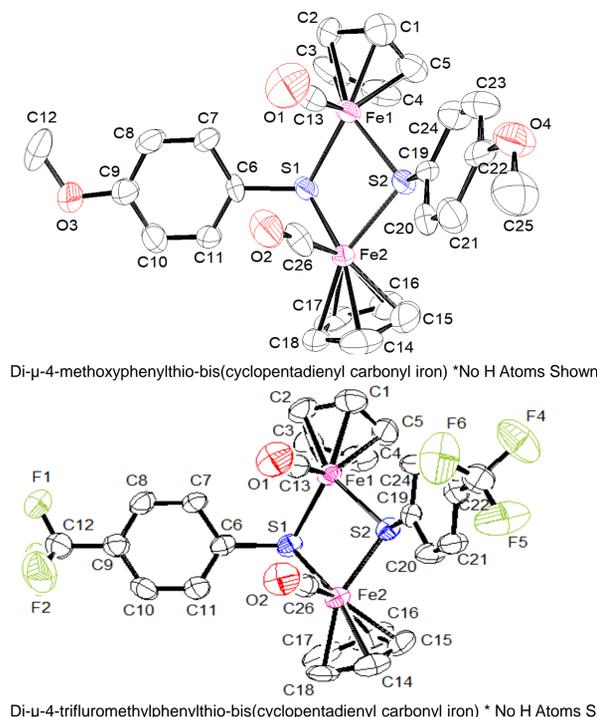
Di-μ-4-methoxyphenylthio-bis(cyclopentadienyl carbonyl iron) *No H Atoms Shown

Di-μ-4-trifluromethylphenylthio-bis(cyclopentadienyl carbonyl iron) * No H Atoms Shown

Discussion

- Two [Fe2 S2] thiolate compounds were synthesized at Cameron University by the same method

  - Thiolate (1) contains the electron-donating group, $-OCH_3$
  - Thiolate (2) contains the electron-withdrawing group, $-CF_3$

- X-ray diffraction data was collected at Cameron University on an Enraf-Nonius CAD-4 Diffractometer employing serial detection at room temperature

- Corresponding bond distances and bond angles for (1) and (2) were compared

  - Fe – S bond distances are net shorter in (1) than those in (2)
  - Fe – C bond distances are net shorter in (1) than those in (2)
  - Fe – S – Fe and S – Fe – S bond angles are net smaller in (1)

Works Cited

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2. Dey, A., Okamura, T., Ueyama, N., Hedman, B., Hodgson, K.O., Solomon, E.I. *Journal of the American Chemical Society* 2005, *127*, 12046
3. McGuire, D.G., Khan, M.A., Ashby, M.T. *Inorganic Chemistry* 2002, *41*, 2202
4. Farrugia, L.J. *J. Appl. Cryst.* 2012, *45*, 849
5. Sheldrick, G.M. *Acta Cryst.* 2002, *A64*, 112

Synthesis

Reaction 1
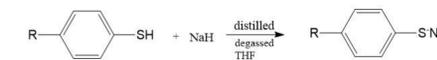
Reaction 2
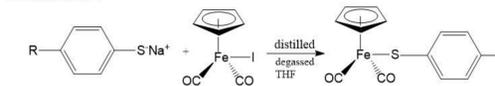
Reaction 3

Where R = OCH_3 and CF_3
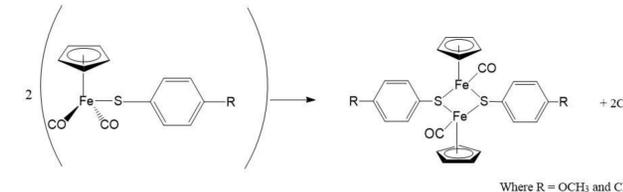
Comparison of Compounds

$[CpFe(CO)(SC_6H_4OCH_3)]_2$	$[CpFe(CO)(SC_6H_4CF_3)]_2$
Bond Distances (Å)	**Bond Distances (Å)**
Fe1-S1 2.269(3)	Fe1-S1 2.276(3)
Fe1-S2 2.278(3)	Fe1-S2 2.261(2)
Fe2-S1 2.266(4)	Fe2-S1 2.273(2)
Fe2-S2 2.263(3)	Fe2-S2 2.271(2)
Fe1-C13 1.745(13)	Fe1-C13 1.770(8)
Fe2-C26 1.745(14)	Fe2-C26 1.745(8)
O1-C13 1.135(13)	O1-C13 1.125(9)
O2-C26 1.144(13)	O2-C26 1.150(9)
Bond Angles (degrees)	**Bond Angles (degrees)**
S1-Fe1-S2 79.08(12)	S1-Fe1-S2 79.74(8)
S1-Fe2-S2 79.44(12)	S1-Fe2-S2 79.57(8)
Fe1-S1-Fe2 97.93(13)	Fe1-S1-Fe2 98.27(9)
Fe1-S2-Fe2 97.75(13)	Fe1-S2-Fe2 98.77(9)
O1-C13-Fe1 176.0(11)	O1-C13-Fe1 178.1(7)
O2-C26-Fe2 178.1(10)	O2-C26-Fe2 177.9(7)

Acknowledgments