*Inorg. Chem.* **1995,** *34,* 5429−5436

# Synthesis of Amphiphilic Metal Organics Using *p*-Monothiohydroquinolate, an Ambidentate Ligand That Bears a Hard and a Soft Donor. One- and Two-Dimensional Solid-State Structures of $Fe_2(CO)_6(\mu\text{-}SC_6H_4\text{-}4\text{-}OH)_2{\cdot}n$Solv (Solv = $C_6H_6$, $n = 1$; Solv = $HSC_6H_4$-4-OH, $n = 2$)[1]

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*Received January 23, 1995*[®]

Triiron dodecacarbonyl reacts with the potential ambidentate ligand 4-hydroxythiophenol (*p*-monothiohydroquinone) to give $Fe_2(CO)_6(\mu\text{-}SC_6H_4\text{-}4\text{-}OH)_2$ (**1**). A preference for binding the soft sulfur donor atom of 4-hydroxythiophenol rather than the hard oxygen donor atom is found when a soft metal and $\pi$-acid ancillary ligands are employed; the amphoteric hydroxy groups of **1** are free to form intermolecular hydrogen bonds. When recrystallized from benzene, **1** yields the benzene solvate $Fe_2(CO)_6(\mu\text{-}SC_6H_4\text{-}4\text{-}OH)_2{\cdot}C_6H_6$, **1**·$C_6H_6$. Derivative **1**·$C_6H_6$ crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$, $a = 10.305(5)$ Å, $b = 11.898(6)$ Å, $c = 12.037(6)$ Å, $\alpha = 102.85(4)°$, $\beta = 95.47(4)°$, $\gamma = 112.06(4)°$, $R = 0.039$, and $R_w = 0.050$ at 20 °C. The structure of **1**·$C_6H_6$ in the solid-state consists of one-dimensional chains of hydrogen-bonded **1**. The hydrophilic groups of adjacent chains face one another; thus the pairs of chains are insulated in one direction by the hydrophobic benzene solvate and in the other by the hydrophobic $Fe_2(CO)_6(S)_2$ moieties. In the presence of excess ligand, **1** forms the ligand solvate $Fe_2(CO)_6(\mu\text{-}SC_6H_4\text{-}4\text{-}OH)_2{\cdot}2HSC_6H_4$-4-OH, **1**·$2HSC_6H_4$-4-OH. Derivative **1**·$2HSC_6H_4$-4-OH crystallizes in the orthorhombic space group $P2_12_12_1$, with $Z = 4$, $a = 8.967(4)$ Å, $b = 12.218(5)$ Å, $c = 31.708(8)$ Å, $R = 0.065$, and $R_w = 0.074$ at 20 °C. The crystal structure of **1**·$2HSC_6H_4$-4-OH consists of chiral two-dimensional nets of annelated 40-membered rings. The nets of **1**·$2HSC_6H_4$-4-OH may be formulated as chains of **1** that are bridged by hydrophilic 4-hydroxythiophenol. The two $Fe_2S_2$ moieties within a given ring are connected by two chains of unequal length, one consisting of 13 covalent bonds and three hydrogen bonds, and the other consisting of 15 covalent bonds and five hydrogen bonds. Furthermore, the two-dimensional nets of **1**·$2HSC_6H_4$-4-OH are not planar; instead, they are folded and stacked to give corrugated layers. Folding the two-dimensional net of **1**·$2HSC_6H_4$-4-OH creates a lamellar superstructure that orients the amphoteric hydroxy groups of **1** within the bilayers (cf. **1**·$C_6H_6$). Thus, the hydrophilic/hydrophobic properties of the molecule of cocrystallization Solv of the **1**·*n*Solv compounds apparently influence the dimensionality of their respective solid-state structures.

## Introduction

Efforts are underway to develop photonic, electronic, and ionic devices that perform highly selective operations for signal and information processing at the molecular level.[2] The eventual utility of such molecular devices will depend on our capability to integrate their constitutional units. Our present ability to manufacture polymolecular assemblies is limited. It will be necessary to exercise control over the supramolecular organization of molecules if devices that operate on the molecular level are to be realized. Many workers have recognized that single crystals offer one possible medium for expression of molecular devices. The repetitiveness of ordered crystals presents the opportunity to amplify molecular properties.[3] As a consequence, the new field of "crystal engineering" has emerged.[4] Hydrogen bonds can influence the solid-state organization of some inorganic and organic crystals[5] and the supramolecular organization of biological molecules.[6] The hydrogen bond might play a similar role in the field of supramolecular coordination chemistry.[7] However, many of the functional groups that might serve a role as hydrogen-bond acceptors are also potential ligands.

The present study demonstrates that hard/soft acid base preferences may be used to facilitate the incorporation of hydrogen-bond acceptor and donor groups into a metal complex in a way that frees them to form intermolecular hydrogen bonds. This study employs the new ligand 4-hydroxythiophenol (or *p*-monothiohydroquinolate). 4-Hydroxythiophenol bears a hard oxygen and a soft sulfur donor group that cannot chelate a single metal atom. When the thiolate group is coordinated to a soft

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[®] Abstract published in *Advance ACS Abstracts,* September 15, 1995.

(1) Presented in part: Ashby, M. T. *Abstracts*; 29th International Conference on Coordination Chemistry, Lausanne, Switzerland; July 19−24, 1992; No. 71.

(2) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* (a) **1988**, *27*, 89−112; (b) **1990**, *29*, 1304 and references therein.

(3) Indeed, this is the way existing single crystal ferroelectric devices function (Jona, F. *Ferroelectric Crystals*; Macmillan: New York, 1962). A ferroelectric crystal is one that has an electric dipole moment even in the absence of an applied electric field. The permanent dipole arises because the center of positive charge in the crystal does not coincide with the center of negative charge. The ferroelectric behavior of many ferroelectric crystals is associated with reorientation of hydrogen bonds (Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; W. A. Benjamin: New York, 1968). The permanent dipole of a ferroelectric crystal may be viewed as an amplification of the molecular dipoles of the individual molecules within the crystal lattice.

(4) Desiraju, G. R. *Crystal Engineering. The Design of Organic Solids;* Elsevier: Amsterdam, 1989.

(5) (a) Etter, M. C.; Frankenbach, G. M. *Chem Mater.* **1989**, *1*, 10. (b) Cao, G.; Hong, H. G.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420. (c) Aakeröy, C. B.; Bahra, G. S.; Hitchcock, P. B.; Patell, Y.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1993**, 152. (d) Copp, S. B.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1078.

0020-1669/95/1334-5429$09.00/0

metal, the amphoteric hydroxy group of 4-hydroxythiophenol is left free to form intramolecular hydrogen bonds.[8] We describe herein the synthesis of *anti*-Fe$_2$(CO)$_6$($\mu$-SC$_6$H$_4$-4-OH)$_2$ (**1**) and the X-ray crystal structures of the two solvates **1**·C$_6$H$_6$ and **1**·2HSC$_6$H$_4$-4-OH. The solid-state structures of the solvate derivatives of **1**, one with a hydrophilic molecule of cocrystallization and the other with a hydrophobic molecule of cocrystallization, offer insight into the influence of the molecule of cocrystallization on the dimensionality of the resulting crystals.

## Experimental Section

All operations were performed under an atmosphere of purified argon using standard Schlenk techniques.[9] Benzene and tetrahydrofuran were dried over Na/benzophenone. Benzene-$d_6$ was dried over molten potassium and then vacuum transferred. Dichloromethane-$d_2$ was vacuum transferred from P$_2$O$_5$. Triiron dodecacarbonyl was synthesized using standard literature procedure.[10] Technical grade 4-hydroxythiophenol containing approximately 10% of the corresponding disulfide was used as received from Aldrich.[11] $^1$H and $^{13}$C NMR spectra were recorded on a Varian XL-300 spectrometer using tetramethylsilane as an internal standard (benzene-$d_6$) or the residual solvent peak (dichloromethane-$d_2$). IR data were collected with a Biorad FTS-7 spectrophotometer. Combustion analyses were performed by Midwest Microlabs, Indianapolis, IN.

**Synthesis of Fe$_2$(CO)$_6$($\mu$-SC$_6$H$_4$-4-OH)$_2$·C$_6$H$_6$, 1·C$_6$H$_6$.** A solution of triiron dodecacarbonyl (600 mg, 1.2 mmol) and 4-hydroxythiophenol (940 mg, 7.5 mmol) in tetrahydrofuran (50 mL) was refluxed for 2 h, during which time the solution turned from green to red. The volatiles were removed under vacuum to give a red/brown oil. The oil was triturated with dry pentane (ca. 100 mL) until it solidified into a dark yellow mass (450 mg). An ether solution (2 mL) of the yellow product (100 mg) was filtered through a short column (5 × 10 mm) of Florisil, the column was washed with ether (1 mL), the combined ether solutions were evaporated to dryness under vacuum, and the resulting red oil was dissolved in a minimum amount of hot benzene (ca. 1 mL), which upon cooling yielded red crystals of **1**·C$_6$H$_6$ (71 mg, about 30% based on Fe). $^1$H NMR (300 MHz, C$_6$D$_6$, 20 °C, TMS): $\delta$ 6.09, 6.95 (d, 8 H, $J$ = 8.5 Hz); 6.18, 7.10 (d, 8 H, $J$ = 8.6 Hz); 7.15 (s, 6 H, benzene). $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$, 20 °C): $\delta$ 115.8, 115.9, 128.7, 130.2, 133.5, 134.2, 135.5, 155.8, 156.2, 208.9. IR (KBr): 2072, 2038, 2002, 1982 cm$^{-1}$. MS (EI 70 eV): $m/z$ 530 ([Fe$_2$(CO)$_6$($\mu$-SC$_6$H$_4$-4-OH)$_2$]$^+$, 2%), 474 ([Fe$_2$(CO)$_4$(SC$_6$H$_4$-4-OH)$_2$]$^+$, 3%), 446 ([Fe$_2$(CO)$_3$(SC$_6$H$_4$-4-OH)$_2$]$^+$, 2%), 418 ([Fe$_2$(CO)$_2$(SC$_6$H$_4$-4-OH)$_2$]$^+$, 2%), 390 ([Fe$_2$(CO)(SC$_6$H$_4$-4-OH)$_2$]$^+$, 2%), 362 ([Fe$_2$(SC$_6$H$_4$-4-OH)$_2$]$^+$, 33%), 126 ([HSC$_6$H$_4$-4-OH]$^+$, 100%). The presence of benzene in the crystal lattice was also demonstrated by X-ray diffraction.

**Table 1.** Crystallographic Data for Fe$_2$(CO)$_6$($\mu$-SC$_6$H$_4$-4-OH)$_2$·$n$Solv (Solv = C$_6$H$_6$, $n$ = 1; Solv = HSC$_6$H$_4$-4-OH, $n$ = 2), **1**·$n$Solv[a]

| | **1**·C$_6$H$_6$ | **1**·2HSC$_6$H$_4$-4-OH |
|---|---|---|
| formula | C$_{24}$H$_{16}$O$_8$S$_2$Fe$_2$ | C$_{30}$H$_{22}$O$_{10}$S$_4$Fe$_2$ |
| fw | 608.21 | 782.46 |
| $T$, K | 293 | 293 |
| space group | $P\bar{1}$ (No. 2) | $P2_12_12_1$ (No. 19) |
| $a$, Å | 10.305(5) | 8.967(4) |
| $b$, Å | 11.898(6) | 12.218(5) |
| $c$, Å | 12.037(6) | 31.708(8) |
| $\alpha$, deg | 102.85(4) | |
| $\beta$, deg | 95.47(4) | |
| $\gamma$, deg | 112.06(4) | |
| $V$, Å$^3$ | 1307.2(13) | 3474(2) |
| $Z$ | 2 | 4 |
| $\lambda$, Å | 0.710 73 | 0.710 73 |
| $\varrho_{\text{calcd}}$, g cm$^{-3}$ | 1.54 | 1.50 |
| $\mu$, cm$^{-1}$ | 13.4 | 11.4 |
| $R$ | 0.039 | 0.065 |
| $R_w$ | 0.050 | 0.074 |

[a] The standard deviation of the least significant figure is given in parentheses in this and subsequent tables. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, GOF $= [\Sigma(w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

**Synthesis of Fe$_2$(CO)$_6$($\mu$-SC$_6$H$_4$-4-OH)$_2$·2HSC$_6$H$_4$-4-OH, 1·2HSC$_6$H$_4$-4-OH.** Red crystals of **1**·2HSC$_6$H$_4$-4-OH suitable for analysis by X-ray diffraction were obtained from a hot toluene solution (2 mL) of **1**·C$_6$H$_6$ (100 mg) containing excess 4-hydroxythiophenol (100 mg). Although this synthesis has been successfully repeated several times, it is not reliable. On average, clean samples of **1**·2HSC$_6$H$_4$-4-OH are obtained about one-third of the time.[12] $^1$H NMR (300 MHz, C$_6$D$_6$, 20 °C, TMS): $\delta$ 6.09, 6.95 (d, 2 H, $J$ = 8.5 Hz); 6.18, 7.10 (d, 2 H, $J$ = 8.6 Hz); 6.32, 6.95 (d, 4 H, $J$ = 8.7 Hz, free HSC$_6$H$_4$-4-OH). Anal. Calcd for C$_{30}$H$_{22}$O$_{10}$S$_4$Fe$_2$ (782.46 g mol$^{-1}$): C, 46.05; H, 2.83; S, 16.39. Found: C, 46.44; H, 2.62; S, 16.20.

**General Procedures Employed in the Crystallographic Studies.** X-ray data were collected with an Enraf-Nonius CAD-4 diffractometer using monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å) and methods standard in this laboratory.[13] The crystallographic data are summarized in Table 1. The positional parameters of the non-hydrogen atoms for **1**·C$_6$H$_6$ and **1**·2HSC$_6$H$_4$-4-OH are given in Tables 2 and 3, respectively. Automatic centering, indexing, and least-squares routines were employed to obtain the cell dimensions. The Laue symmetry and systematic absences of trial data sets were used to identify the space groups. The data were corrected for Lorentz and polarization effects, but no absorption correction was applied since it was judged to be negligible. The structures were solved using a combination of the heavy atom and direct methods provided by the SHELX-86 program.[14] Neutral scattering factors were used for all atoms.[15] The models were refined using the SHELX-76 program and full-matrix methods.[16]

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(6) Information gathering, amplification, and processing at the molecular level requires inter device communication. Nature has provided us with an outstanding precedent for using hydrogen-bonded networks for such communication. It is postulated that *in vivo* photosynthesis involves hundreds of chlorophyll molecules that work in concert as an "antenna" to capture photons and pass the energy along to the reaction center. One important model for the antenna has the chlorophyll molecules chained together with hydrogen bonds (Chow, H.-C.; Serlin, R.; Strouse, C. E. *J. Am. Chem. Soc.*, **1975**, *97*, 7230. Scheer, H., Ed. *Chlorophylls*; CRC Press: Boca Raton, FL, 1991).

(7) See the following references for recent examples of metal-containing extended assemblies. Metallo-organic double helices: Lehn, J.-M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevier, B.; Moras, D. *Proc. Nat. Acad. Sci. U.S.A.* **1987**, *84*, 2565. Koert, U.; Harding, M. M.; Lehn, J.-M. *Nature*, **1990**, *349*, 339. Williams, A. F.; Piguet, C.; Bernardinelli, G. *Angew. Chem., Int Ed. Engl.* **1991**, *30*, 1490. Metal surfaces: Häussling, L.; Michel, B.; Ringsdorf, H.; Roher, H. *Angew. Chem., Int Ed. Engl.* **1991**, *30*, 569. Pale Grosdemange, C.; Simon, E. S.; Prime, K. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 12. Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152. Transition metal chelates: Schepartz, A.; McDevitt, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 5976. Saalfrank, R. W.; Stark, A.; Bremer, M.; Hummel, H.-U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 311. Metal-assisted organization of macrocyclic hosts: Kobuke, Y.; Sumida, Y.; Hayashi, M.; Ogoshi, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1496. Vesicle formation by an amphiphilic metallo-organic derivatives: Medina, J. C.; Gay, I.; Chen, Z.; Echegoyen, L.; Gokel, G. W. *J. Am. Chem. Soc.*, **1991**, *113*, 365.

(8) ($\eta^5$-C$_5$H$_5$)Fe(CO)$_2$(SC$_6$H$_4$-4-OH) and ($\eta^5$-C$_5$H$_5$)Mo(NO)(SC$_6$H$_4$-4-OH)$_2$ may be synthesized from the corresponding halides: Ashby, M. T. Unpublished results.

(9) *Organometallic Compounds*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

(10) McFarlane,W.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 181.

(11) The corresponding disulfide may be used instead of the thiol in this synthesis with similar results.

(12) The reason behind the poor reliability of this synthetic procedure is not entirely clear but appears to be due to the fact that crystallization is a kinetic phenomenon that can been inhibited by the presence of impurities and some decomposition of **1** takes place during the recrystallization. Thus the recrystallization competes with decomposition.

(13) Ashby, M. T.; Khan, M. A.; Halpern, J. *Organometallics* **1991**, *10*, 2011.

(14) Sheldrick, G. M. *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175–189.

**Table 2.** Atomic Coordinates and Equivalent Isotropic Thermal Parameters[a] (Å$^2$) for **1**·$C_6H_6$

| atom | *x*/*a* | *y*/*b* | *z*/*c* | $U_{eq}$ |
|---|---|---|---|---|
| Fe1 | 0.43124(7) | 0.61037(6) | 0.76831(6) | 0.0599(3) |
| Fe2 | 0.30610(8) | 0.67314(6) | 0.92547(5) | 0.0588(3) |
| S1 | 0.50402(13) | 0.81161(11) | 0.8850(1) | 0.0600(5) |
| S2 | 0.22873(12) | 0.64089(10) | 0.73504(9) | 0.0454(4) |
| C11 | 0.4766(5) | 0.9118(4) | 0.8027(4) | 0.0485(8) |
| C12 | 0.3624(5) | 0.9457(4) | 0.7997(4) | 0.0568(9) |
| C13 | 0.3517(5) | 1.0254(4) | 0.7333(4) | 0.0593(9) |
| C14 | 0.4574(5) | 1.0716(4) | 0.6709(4) | 0.0505(8) |
| C15 | 0.5724(5) | 1.0387(4) | 0.6759(4) | 0.0547(9) |
| C16 | 0.5822(5) | 0.9590(4) | 0.7416(4) | 0.0545(8) |
| O1 | 0.4405(4) | 1.1471(3) | 0.6059(3) | 0.0677(8) |
| C21 | 0.0675(4) | 0.5032(4) | 0.6708(3) | 0.0437(8) |
| C22 | 0.0601(4) | 0.4136(4) | 0.5720(3) | 0.0467(8) |
| C23 | −0.0706(4) | 0.3161(4) | 0.5136(3) | 0.0492(8) |
| C24 | −0.1927(5) | 0.3110(4) | 0.5536(3) | 0.0480(8) |
| C25 | −0.1872(5) | 0.3989(4) | 0.6526(4) | 0.0564(9) |
| C26 | −0.0569(5) | 0.4948(4) | 0.7111(4) | 0.0538(8) |
| O2 | −0.3241(3) | 0.2188(3) | 0.4956(3) | 0.0644(8) |
| C3 | 0.4922(5) | 0.6281(5) | 0.6341(5) | 0.0758(9) |
| O3 | 0.5284(5) | 0.6384(4) | 0.5496(4) | 0.1109(9) |
| C4 | 0.5885(6) | 0.6087(5) | 0.8397(6) | 0.0974(9) |
| O4 | 0.6910(5) | 0.6080(4) | 0.8865(5) | 0.1449(9) |
| C5 | 0.3394(5) | 0.4417(5) | 0.7311(5) | 0.0754(9) |
| O5 | 0.2819(4) | 0.3347(3) | 0.7097(4) | 0.1038(8) |
| C6 | 0.2200(6) | 0.7667(5) | 0.9939(4) | 0.0743(9) |
| O6 | 0.1636(5) | 0.8277(4) | 1.0351(4) | 0.1112(9) |
| C7 | 0.4190(7) | 0.6760(5) | 1.0492(5) | 0.1010(9) |
| O7 | 0.4897(6) | 0.6727(4) | 1.1259(4) | 0.1527(9) |
| C8 | 0.1776(6) | 0.5233(5) | 0.9273(4) | 0.0746(9) |
| O8 | 0.0971(5) | 0.4276(4) | 0.9286(3) | 0.1041(9) |
| C31 | 0.1170(6) | 0.1817(5) | 0.3116(4) | 0.064(1) |
| C32 | 0.0412(6) | 0.1134(5) | 0.1987(4) | 0.088(1) |
| C33 | −0.0185(6) | −0.0184(5) | 0.1671(4) | 0.113(1) |
| C34 | −0.0025(6) | −0.0818(5) | 0.2483(4) | 0.098(1) |
| C35 | 0.0732(6) | −0.0136(5) | 0.3612(4) | 0.089(1) |
| C36 | 0.1330(6) | 0.1182(5) | 0.3928(4) | 0.071(1) |
| C31′ | 0.0709(7) | 0.1474(6) | 0.2480(5) | 0.122(1) |
| C32′ | −0.0079(7) | 0.0323(6) | 0.1643(5) | 0.113(1) |
| C33′ | −0.0311(7) | −0.0808(6) | 0.1917(5) | 0.093(1) |
| C34′ | 0.0246(7) | −0.0787(6) | 0.3028(5) | 0.098(1) |
| C35′ | 0.1034(7) | 0.0364(6) | 0.3865(5) | 0.121(1) |
| C36′ | 0.1265(7) | 0.1495(6) | 0.3591(5) | 0.132(1) |

[a] Equivalent isotropic thermal parameter ($U_{eq}$) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Crystal Data for 1·$C_6H_6$.** The crystallographic data for **1**·$C_6H_6$ are summarized in Table 1. The Laue symmetry and systematic absences of a trial data set unambiguously determined the cell to be triclinic and the space group to be $P\bar{1}$. A total of 3394 unique reflections was measured ($3 \leq 2\theta \leq 50°$). The heavy atoms and the aromatic hydrogen atoms (in calculated positions) were included in the final refinement. All of the heavy atoms of the **1** moiety were refined anisotropically. The benzene solvate is disordered. C19−C24 and C19′−C24′ represent a disorder model for the benzene solvate that consists of two regular hexagons with 0.5 occupancy each. The molecules are defined by 24 parameters: two point, two rotation matrices of three vectors, and two sets of six isotropic thermal parameters. Full-matrix least-squares refinement with 2564 observed reflections ($|F_o| \geq 2\sigma|F_o|$) and 235 variables converged to give $R = 0.039$, $R_w = 0.050$, GOF = 2.63, and final residual = 0.41 e Å$^{-3}$.

**Table 3.** Atomic Coordinates and Isotropic Thermal Parameters (Å$^2$) for **1**·2HS$C_6H_4$-4-OH

| atom | *x*/*a* | *y*/*b* | *z*/*c* | *U* |
|---|---|---|---|---|
| Fe1 | 0.5985(3) | 0.8040(2) | 0.21945(8) | 0.0380(7)[a] |
| Fe2 | 0.8546(3) | 0.8601(2) | 0.24224(8) | 0.0365(7)[a] |
| S1 | 0.7805(5) | 0.6834(3) | 0.2388(1) | 0.039(1)[a] |
| C11 | 0.841(2) | 0.610(1) | 0.1940(5) | 0.025(3) |
| C12 | 0.974(2) | 0.624(1) | 0.1725(5) | 0.050(4) |
| C13 | 1.017(2) | 0.561(1) | 0.1380(5) | 0.056(4) |
| C14 | 0.919(2) | 0.480(2) | 0.1252(6) | 0.049(4) |
| C15 | 0.789(2) | 0.458(2) | 0.1469(6) | 0.047(4) |
| C16 | 0.751(2) | 0.524(2) | 0.1794(6) | 0.046(4) |
| O1 | 0.955(1) | 0.412(1) | 0.0920(4) | 0.056(3) |
| S2 | 0.7819(5) | 0.8512(4) | 0.1743(1) | 0.034(1)[a] |
| C21 | 0.765(2) | 0.979(1) | 0.1478(5) | 0.034(3) |
| C22 | 0.881(2) | 1.054(1) | 0.1507(6) | 0.042(4) |
| C23 | 0.878(2) | 1.147(2) | 0.1248(6) | 0.041(4) |
| C24 | 0.762(2) | 1.164(2) | 0.0982(6) | 0.045(4) |
| C25 | 0.647(2) | 1.091(1) | 0.0946(6) | 0.047(4) |
| C26 | 0.647(2) | 0.998(1) | 0.1200(5) | 0.047(4) |
| O2 | 0.758(1) | 1.254(1) | 0.0728(4) | 0.054(3) |
| C3 | 0.473(2) | 0.721(2) | 0.1886(6) | 0.065(4) |
| O3 | 0.397(2) | 0.664(1) | 0.1705(5) | 0.084(4) |
| C4 | 0.513(2) | 0.786(1) | 0.2694(5) | 0.061(4) |
| O4 | 0.458(2) | 0.774(1) | 0.3019(5) | 0.085(4) |
| C5 | 0.507(2) | 0.929(1) | 0.2115(6) | 0.048(4) |
| O5 | 0.449(2) | 1.014(1) | 0.2076(5) | 0.073(3) |
| C6 | 1.055(2) | 0.861(2) | 0.2382(7) | 0.046(4) |
| O6 | 1.180(2) | 0.861(1) | 0.2349(5) | 0.073(3) |
| C7 | 0.839(2) | 0.844(2) | 0.2958(6) | 0.039(4) |
| O7 | 0.821(2) | 0.832(1) | 0.3318(5) | 0.080(4) |
| C8 | 0.822(2) | 1.003(1) | 0.2436(6) | 0.044(4) |
| O8 | 0.795(2) | 1.094(1) | 0.2482(5) | 0.070(4) |
| S3 | 1.1745(9) | 0.8257(6) | −0.0778(2) | 0.098(2)[a] |
| C31 | 1.186(2) | 0.716(2) | −0.0436(7) | 0.071(4) |
| C32 | 1.073(3) | 0.704(2) | −0.0129(7) | 0.079(5) |
| C33 | 1.083(2) | 0.621(2) | 0.0173(7) | 0.070(4) |
| C34 | 1.190(2) | 0.547(2) | 0.0165(7) | 0.069(4) |
| C35 | 1.307(2) | 0.554(2) | −0.0124(7) | 0.066(4) |
| C36 | 1.298(2) | 0.642(2) | −0.0418(6) | 0.065(4) |
| O9 | 1.194(2) | 0.463(1) | 0.0466(5) | 0.077(4) |
| S4 | 0.215(1) | 0.8597(7) | 0.1102(3) | 0.110(2)[a] |
| C41 | 0.230(2) | 0.983(2) | 0.0804(7) | 0.058(4) |
| C42 | 0.223(3) | 0.979(2) | 0.0376(7) | 0.075(5) |
| C43 | 0.232(3) | 1.073(2) | 0.0137(8) | 0.081(5) |
| C44 | 0.254(2) | 1.174(2) | 0.0345(7) | 0.073(5) |
| C45 | 0.263(2) | 1.177(2) | 0.0780(6) | 0.061(4) |
| C46 | 0.253(2) | 1.082(2) | 0.1007(7) | 0.067(4) |
| O10 | 0.280(2) | 1.271(1) | 0.0144(5) | 0.088(4) |

[a] Equivalent isotropic thermal parameter ($U_{eq}$), which is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Crystal Data for 1·2HS$C_6H_4$-4-OH.** The crystallographic data for **1**·2HS$C_6H_4$-4-OH are summarized in Table 1. Finding a crystal suitable for the X-ray diffraction study proved to be difficult. Many of the plate-like crystals were disordered along the small dimension (*c* axis). This external morphology is consistent with the two-dimensional lamellar organization in the solid-state structure (*vide infra*). The Laue symmetry and systematic absences of a trial data set unambiguously determined the cell to be orthorhombic and the space group to be $P2_12_12_1$. A total of 3503 unique reflections was measured ($3 \leq 2\theta \leq 50°$). The SHELX-86 program has direct methods for non-centrosymmetric space groups that proved to be particularly helpful in solving the structure. The heavy atoms and the aromatic hydrogen atoms (in calculated positions) were included in the final refinement. Because of the limited amount of observed data, only the iron and sulfur atoms were refined anisotropically. Full-matrix least-squares refinement with 1867 observed reflections ($|F_o| \geq 3\sigma|F_o|$) and 231 variables converged to give $R = 0.065$, $R_w = 0.074$, GOF = 3.87, and final residual = 0.55 e Å$^{-3}$. Attempts to recollect the diffraction data at low temperatures failed because the crystals fractured upon cooling.

## Results

Triiron dodecacarbonyl reacts with 4-hydroxythiophenol (or *p*-monothiohydroquinolate) selectively with the thiol rather than the hydroxy group to give thiolate-bridged dimers with the formula $Fe_2(CO)_6(\mu\text{-}SC_6H_4\text{-}4\text{-}OH)_2$, **1**. There are three possible stereoisomers of **1**; however, only isomer **1a** has been isolated (Figure 1):

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(15) *International Tables for X-ray Crystallography*, Kynoch Press: Birmingham, England,1974; Vol. IV; pp 99, 149.

(16) *SHELX-76. Program for Crystal Structure Determination*; University of Chambridge: Chambridge, England, 1976.

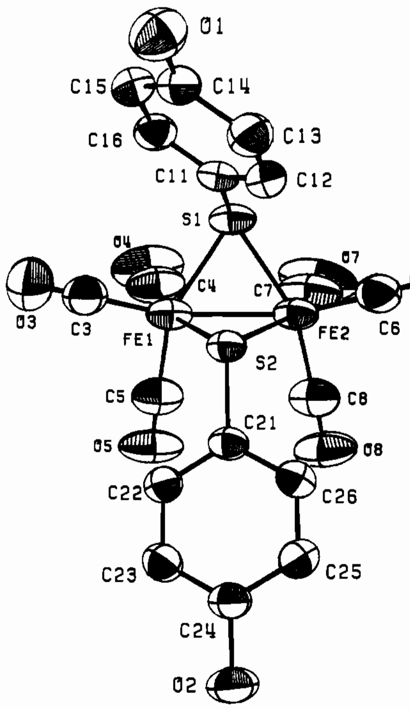
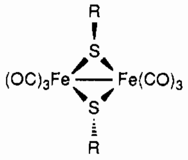
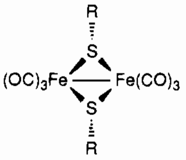


**Figure 1.** Thermal ellipsoid plot (50% level) and atom labeling scheme of the **1** moiety of **1**·$C_6H_6$. The hydrogen atoms have been omitted for clarity in this and subsequent figures.



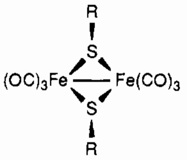
anti

**1a**



syn-endo

**1b**



syn-exo

**1c**

To our knowledge, compound **1** represents the first metal complex of the ambidentate ligand 4-hydroxythiophenolate to be characterized. Because it possesses two binding sites, one a hard oxygen and the other a soft sulfur donor, the ligand should exhibit affinity toward both hard and soft metals.[17] Compound **1** bears soft $Fe^I$ metals that are bound by symbiotic[18] carbonyl ligands that further soften the metal centers. Accordingly, the 4-hydroxythiophenolate ligands are sulfur-bound. This leaves the hydroxy groups free to form hydrogen bonds (*vide infra*).

When **1** is crystallized from hot benzene, the solvate $Fe_2(CO)_6(\mu\text{-}SC_6H_4\text{-}4\text{-}OH)_2{\cdot}C_6H_6$, **1**·$C_6H_6$, is formed. The crystal structure of **1**·$C_6H_6$ demonstrates that the **1** moiety of **1**·$C_6H_6$ adopts *anti* stereochemistry (**1a**), as was inferred from the $^1H$ NMR spectra of **1**. The structure of **1**·$C_6H_6$ in the solid-state consists of one-dimensional chains of hydrogen-bonded **1** (Figure 1 for the labeling scheme, Figure 3 for elevations of the chains showing the hydrogen bonds, and Figure 5 for a space-filled stereoview of the lattice). The hydrophilic groups of adjacent chains face one another; thus the chains are insulated in one direction by the hydrophobic benzene solvate and in the other by the hydrophobic $Fe_2(CO)_6(S)_2$ moieties (Figures 3 and 5).[19] However, it does not appear that hydrogen bonds bridge the adjacent chains as might be expected from the ribbon-like appearance of **1**·$C_6H_6$ (*vide infra*). Table 4 summarizes selected interatomic distances and angles of **1**·$C_6H_6$. Table 5 summarizes the geometries about the hydrogen bonds of **1**·$C_6H_6$. The distances and angles of **1** moiety of **1**·$C_6H_6$ are comparable to those observed for analogous *anti*-$Fe_2(CO)_6(\mu\text{-}SR)_2$ compounds.[20] The quality of the crystal structure precluded location of the hydrogen atoms that are involved in hydrogen bonding; however, intermolecular hydrogen bonding is indicated by the fact that the oxygen atoms of the hydroxy groups of adjacent molecules are within the sum of their van der Waals radii. The observed O1···O2′ distance of 2.817(5) Å is within the normal range of 2.6–2.8 Å for strong OH···O′ hydrogen bonds.[21] Furthermore, the geometries about the oxygen atoms, as indicated by the C–O···O′ angles of 108.1(3) and 122.2(3)°, suggest a linear hydrogen bond, which is the optimum geometry for a hydrogen bond. Although the hydrophilic groups of adjacent chains face one another, and in some cases the intermolecular O-atom contacts are less than 3 Å, only the hydrogen bonds that are indicated in Figure 3 exhibit ideal geometry (i.e. are approximately linear).

**Table 4.** Selected Interatomic Distances (Å) and Angles (deg) for **1**·$C_6H_6$ and **1**·$2HSC_6H_4$-4-OH

| | **1**·$C_6H_6$ | **1**·$2HSC_6H_4$-4-OH | | **1**·$C_6H_6$ | **1**·$2HSC_6H_4$-4-OH |
|---|---|---|---|---|---|
| Fe1–Fe2 | 2.522(1) | 2.504(3) | Fe2–S1 | 2.266(1) | 2.262(5) |
| Fe1–S1 | 2.286(1) | 2.282(4) | Fe2–S2 | 2.251(1) | 2.254(5) |
| Fe1–S2 | 2.263(1) | 2.254(5) | Fe2–C6 | 1.783(5) | 1.80(2) |
| Fe1–C3 | 1.815(6) | 1.80(2) | Fe2–C7 | 1.787(6) | 1.72(2) |
| Fe1–C4 | 1.770(6) | 1.77(2) | Fe2–C8 | 1.784(5) | 1.77(2) |
| Fe1–C5 | 1.794(5) | 1.76(2) | | | |
| Fe1–S1–Fe2 | 67.29(4) | 66.9(1) | S1–Fe2–C7 | 87.5(2) | 85.2(7) |
| Fe1–S2–Fe2 | 67.92(4) | 67.5(2) | S1–Fe2–C8 | 157.4(2) | 153.2(6) |
| S1–Fe1–S2 | 79.71(5) | 79.3(2) | S2–Fe2–C6 | 102.9(2) | 102.9(7) |
| S1–Fe2–S2 | 80.39(5) | 79.8(2) | S2–Fe2–C7 | 155.7(2) | 156.5(7) |
| S1–Fe1–C3 | 105.3(2) | 103.4(6) | S2–Fe2–C8 | 93.3(2) | 91.4(6) |
| S1–Fe1–C4 | 97.3(2) | 89.4(5) | C3–Fe1–C4 | 96.2(3) | 98.5(8) |
| S1–Fe1–C5 | 154.6(2) | 159.5(6) | C3–Fe1–C5 | 100.0(2) | 96.7(8) |
| S2–Fe1–C3 | 99.2(2) | 104.7(6) | C4–Fe1–C5 | 92.4(2) | 91.9(8) |
| S2–Fe1–C4 | 161.9(2) | 156.0(6) | C6–Fe2–C7 | 100.6(2) | 98.8(9) |
| S2–Fe1–C5 | 94.1(2) | 91.5(6) | C6–Fe2–C8 | 97.3(2) | 99.4(9) |
| S1–Fe2–C6 | 105.3(2) | 107.3(7) | C7–Fe2–C8 | 89.9(2) | 94.1(9) |

**Table 5.** Geometries about the Hydrogen Bonds of **1**·$C_6H_6$ and **1**·$2HSC_6H_4$-4-OH[a]

| | | | |
|---|---|---|---|
| Geometry about the Chains of **1** in **1**·$C_6H_6$ | | | |
| O1–C14 | 1.362(5) | C14–O1···O2′ | 108.1(3) |
| O2–C24 | 1.374(5) | O1···O2′–C24′ | 122.2(3) |
| O1···O2′ | 2.817(5) | C14–O1···O2′–C24′ | 77.4(4) |
| Geometry about the Chains of **1** in **1**·$2HSC_6H_4$-4-OH | | | |
| O1–C14 | 1.38(2) | C14–O1···O2′ | 111(1) |
| O2–C24 | 1.37(2) | O1···O2′–C24′ | 115(1) |
| O1···O2′ | 2.69(2) | C14–O1···O2′–C24′ | 79(2) |
| Geometry about the Chains of **1** and $HSC_6H_4$-4-OH in **1**·$2HSC_6H_4$-4-OH | | | |
| O1–C14 | 1.38(2) | C14–O1···O9 | 117(1) |
| O9–C34 | 1.40(3) | O1···O9–C34 | 121(1) |
| O1···O9 | 2.66(2) | C14–O1···O9–C34 | 77(2) |
| O2–C24 | 1.37(2) | C24–O2···O10 | 119(1) |
| O10–C44 | 1.37(3) | O2···O10–C44 | 109(1) |
| O2···O10 | 2.79(2) | C24–O2···O10–C44 | 172(2) |
| O9–C34 | 1.40(3) | C34–O9···O10 | 112(1) |
| O10–C44 | 1.36(3) | O9···O10–C44 | 122(1) |
| O9···O10 | 2.68(2) | C34–O9···O10–C44 | 162(2) |

[a] Distances in Å; angles in deg.

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(17) Pearson, R. G. *Hard and Soft Acids and Bases*; Dowden, Hutchinson, & Ross: Stroudsburg, PA, 1973.

(18) Jørgensen, C. K. *Inorg. Chem.* **1964**, *3*, 1201.

(19) Since $Fe_2(CO)_6X_2$ complexes are in general insoluble in water, we conclude that they are hydrophobic.

(20) (a) Henslee, W.; Davis, R. E. *Cryst. Struct. Commun.* **1972**, *1*, 403. (b) Katser, S. B.; Antsyshkina, A. S.; Katugin, A. S.; Abdullaev, A. S. *Koord. Khim.* **1987**, *13*, 1132.

(21) Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91.

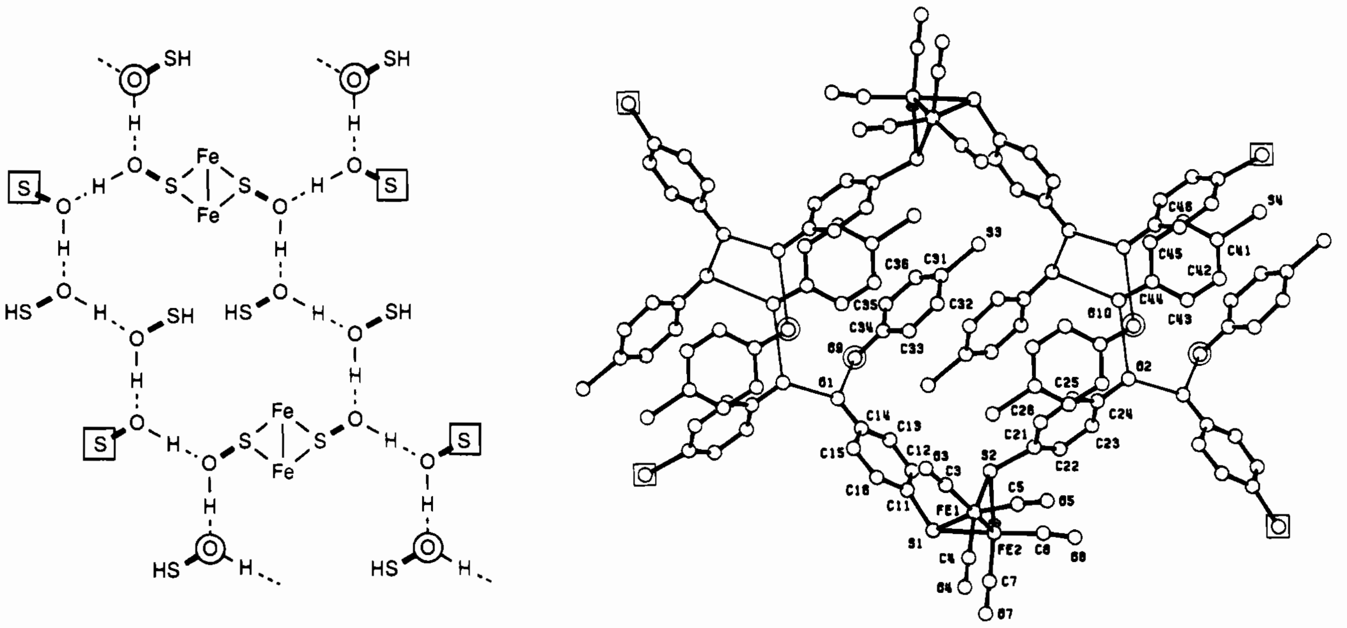


**Figure 2.** Diagrammatic illustration (left) and ORTEP drawing with labeling scheme (right) of the 40-membered ring of 1·$2HSC_6H_4$-4-OH. The heavy atoms have been assigned arbitrary thermal parameters. Covalent and coordination bonds are represented with thick lines and hydrogen bonds are represented with thin lines.

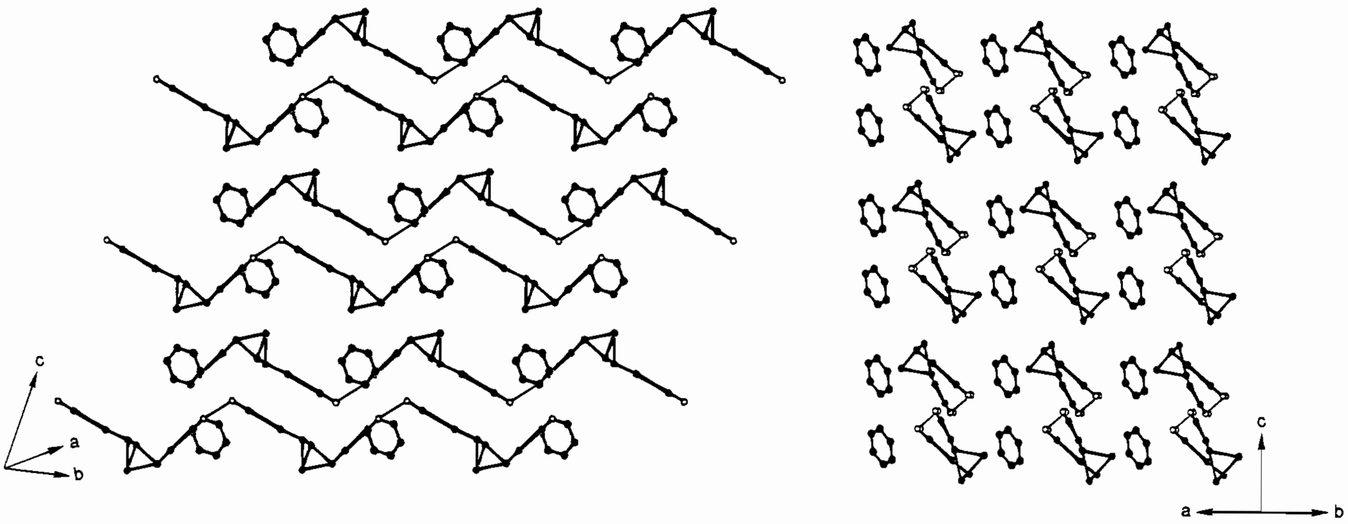


**Figure 3.** Elevation of portions of three ribbons of 1·$C_6H_6$. Hydrogen atoms and carbonyl ligands have been omitted for clarity. Phenyl groups are represented with bold lines and hydrogen bonds are represented by thin lines. The elevation on the left is a side-on depiction of the chains of **1** as viewed down the bisect of the $-a$ and $b$ axes. The elevation on the right is an end-on depiction of the chains of **1** as viewed down the bisect of the $a$ and $b$ axes. Note that the ribbons of two chains of **1** are insulated by the carbonyl ligands in one direction and the hydrophobic benzene solvate in the other direction.

Compound **1** cocrystallizes with excess 4-hydroxythiophenol to form $Fe_2(CO)_6(\mu\text{-}SC_6H_4\text{-}4\text{-}OH)_2\cdot 2HSC_6H_4\text{-}4\text{-}OH$, **1**·$2HSC_6H_4$-4-OH. The role of the two "ligands of crystallization" became apparent when the solid-state structure of **2** was determined by single-crystal X-ray crystallography. Selected interatomic distances and angles of **1**·$2HSC_6H_4$-4-OH are summarized in Table 4. The **1** moiety of **1**·$2HSC_6H_4$-4-OH also adopts the stereochemistry of **1a** (Figure 2). Again, the distances and angles of the **1** moiety of **1**·$2HSC_6H_4$-4-OH are comparable to those observed for analogous *anti*-$Fe_2(CO)_6(\mu\text{-}SR)_2$ compounds.[20] The quality of the crystal structure once again precluded location of the hydrogen atoms of the hydroxy groups, but hydrogen bonding can be inferred from the geometries about the oxygen atoms of the hydroxy groups. The geometries about the hydrogen bonds of **1**·$2HSC_6H_4$-4-OH are summarized in Table 5. The structure of **1**·$2HSC_6H_4$-4-OH consists of chiral two-dimensional nets of annelated 40-membered rings (Figure 1 for the labeling scheme, Figure 2 for a view of the 40-member ring, Figure 4 for elevations of the layers showing the hydrogen bonds, and Figure 6 for a space-filled stereoview of the lattice). Interestingly, the rings (which nominally contain eight hydrogen bonds) are not symmetric. The two $Fe_2S_2$ moieties within a given ring are connected by two chains of unequal length, one consisting of thirteen covalent bonds and three hydrogen bonds, and the other consisting of fifteen covalent bonds and five hydrogen bonds. Furthermore, the two-dimensional nets of **1**·$2HSC_6H_4$-4-OH are not planar, rather, they are folded and stacked to give corrugated layers (Figures 4 and 6). The organization of **1**·$2HSC_6H_4$-4-OH can also be viewed as chains of **1** not unlike those found for **1**·$C_6H_6$. However, whereas the chains of **1** found in the structure of **1**·$C_6H_6$ do not exhibit an ideal geometry for inter-chain hydrogen bonding, the chains of **1** are linked together by the hydrophilic molecules of cocrystallization.

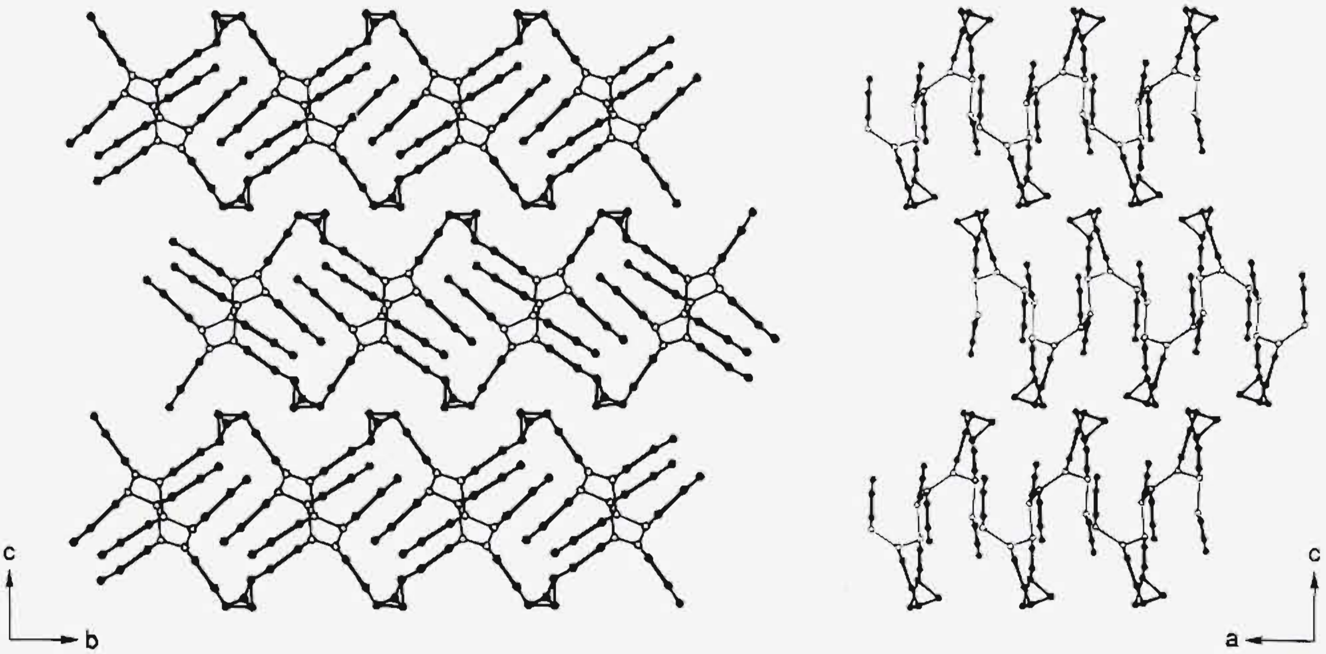


**Figure 4.** Elevation of portions of three layers of **1**·$2HSC_6H_4$-4-OH. Hydrogen atoms and carbonyl ligands have been omitted for clarity. Phenyl groups are represented with bold lines and hydrogen bonds are represented by thin lines. Note the lamellar organization (elevation on the left), with the hydrophilic 4-hydroxythiophenyl molecule of cocrystallization sandwiched between the hydrophilic sides of the chains of **1**. The view on the left is down the a axis and the view on the right is down the b axis.

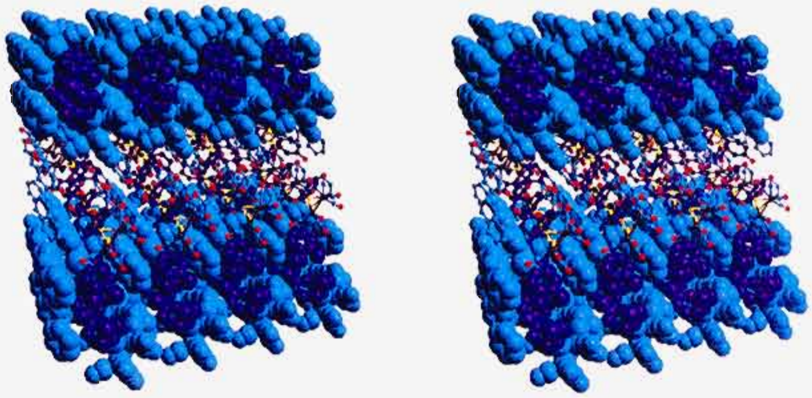


**Figure 5.** HyperChem stereo drawing of three ribbons of **1**·$C_6H_6$. The top and bottom sets of ribbons are represented in space-filled mode with the $Fe_2S_2(CO)_6$ and solvate $C_6H_6$ in light blue (cyan) and the $C_6H_4OH$ moieties in dark blue. The middle set of ribbons is represented in ball-and-stick mode with the colors representing the different types of atoms: carbons of $Fe_2S_2(CO)_6$ and $C_6H_6$ = light blue, carbons of $C_6H_4OH$ = dark blue, oxygen = red, sulfur = yellow, and iron = black.

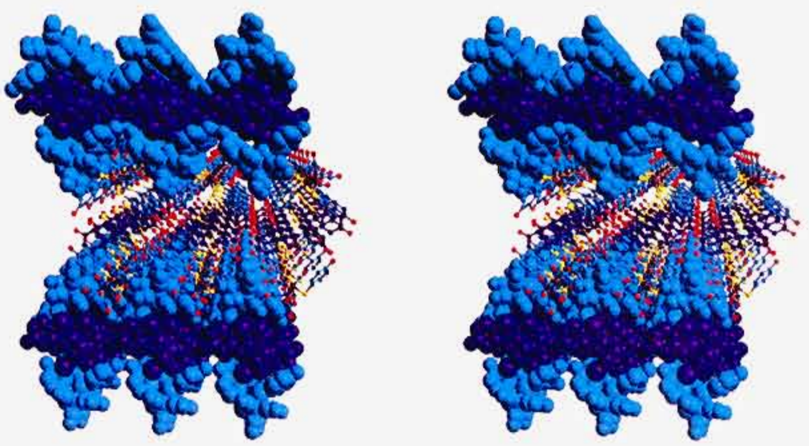
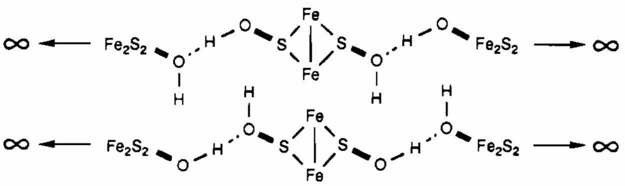


**Figure 6.** HyperChem stereo drawing of three lamellar layers of **1**·$2HSC_6H_4$-4-OH. The top and bottom set of layers are represented in space-filled mode with the **1** moieties in light blue (cyan) and the solvate $HSC_6H_4OH$ moieties in dark blue. The middle layer is represented in ball-and-stick mode with the colors representing the different types of atoms: carbons of **1** = light blue, carbons of $HSC_6H_4OH$ = dark blue, oxygen = red, sulfur = yellow, and iron = black.

## Discussion

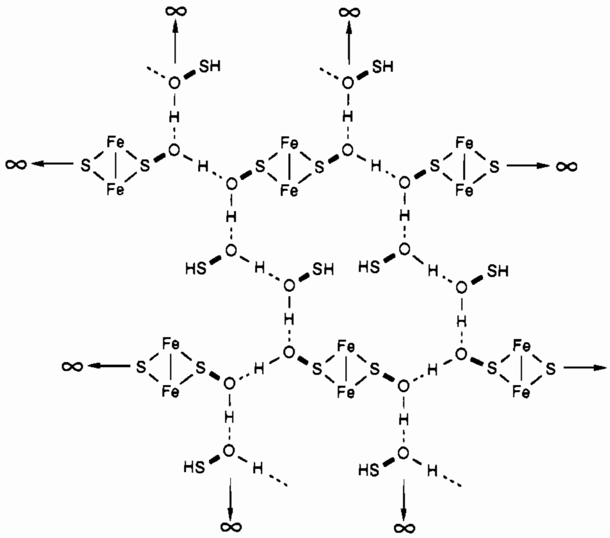
Low-dimensional solids should exhibit one or more properties that reflect their dimensionality.[22] One such property is lattice strength. Molecular solids are usually held together by van der Waals forces, which are weak and nondirectional. Accordingly, molecular solids that do not exhibit significant intermolecular interactions should be considered three-dimensional.[23] The intermolecular hydrogen bonds of **1** are highly directional and are much stronger than a given van der Waals interaction. The dimensionality of a hydrogen-bonded network depends on the nature of its constitutional units.[24] Whereas the ligand itself possesses only one amphoteric group that is capable of forming strong hydrogen bonds (the thiol group does not form strong hydrogen bonds[25]), the metal moiety **1** possesses two groups that are capable of forming strong hydrogen bonds (albeit only intermolecularly). Molecules that bear two amphoteric groups are capable of organizing in many different ways, e.g., cyclic oligomers, one-dimensional chains, one-dimensional ribbons, two-dimensional nets, and three-dimensional nets.[26] However, the possible modes of organization of the hydrogen-bond network will not only be determined by the number of available amphoteric groups, but also by constraints that are inherent in the geometry of the molecule. Compound **1** is highly rigid. In fact, the spacing and geometry of the two amphoteric groups of **1** are fixed. Because of the rigid nature of **1**, certain organizational modes can be deemed unfavorable. For example, we note that a linear arrangement of the hydrogen bonds is not possible for cyclic oligomers and one-dimensional chains of **1**, at least for the case where all of the hydrogen atoms of the hydroxy groups take part in hydrogen bonding. Furthermore, the rigidity of **1** would seem to preclude the formation of three-dimensional nets (*vide infra*). In contrast, one-dimensional ribbons and two-dimensional nets of **1** seem possible wherein all of the hydroxy groups can take part in hydrogen bonding.

It would appear at first that these are the organizational modes that are favored for **1** as indicated by the ribbon-like solid-state structure of **1**·$C_6H_6$ and net-like solid-state structure of **1**·$2HSC_6H_4$-4-OH. However, upon close inspection of the crystal structure of **1**·$C_6H_6$ it appears that the organization of the **1** moieties actually consist of chains of **1** wherein only one hydrogen atom of each hydroxy group propagates the chain and the other is oriented toward an adjacent chain, albeit in a geometry that does not favor interchain hydrogen bonding:



Nonetheless, the chains of **1**·$C_6H_6$ are oriented with their hydophilic groups toward one another.

The organization of **1**·$2HSC_6H_4$-4-OH is comparable to that of **1**·$C_6H_6$, wherein the hydrophobic groups orient themselves toward one another. In fact, the chains of **1** in **1**·$C_6H_6$ and **1**·$2HSC_6H_4$-4-OH are very similar; however, where as the geometry about the chains of **1**·$C_6H_6$ appears to preclude interchain hydrogen bonding, the chains of **1**·$2HSC_6H_4$-4-OH are bridged by 4-hydroxythiophenol. This results is a two-dimensional net (*vide supra*):



We suggest that a one-dimensional structure is found for **1**·$C_6H_6$ because of packing and geometric constrains, as well as the influence of the benzene molecules of cocrystallization, which serve to insulate[27] the adjacent chains from one another thereby preventing the formation of a two-dimensional net. As expected based upon the results obtained for **1**·$C_6H_6$, the 4-hydroxythiophenol molecules of cocrystallization have a marked influence on the organization of the hydrogen bonds of **1**·$2HSC_6H_4$-4-OH. In addition to possible geometric constraints, we note that the two-dimensional nets of **1**·$2HSC_6H_4$-4-OH are corrugated in the lattice and this creates a lamellar superstructure that orients the amphoteric hydroxy groups of **1** within the bilayers. From a descriptive standpoint, the hydrophobic $Fe_2(CO)_6(S)_2$ moieties serve to insulate the bilayers from one another thereby creating a van der Waals gap that is often characteristic of two-dimensional solids. The cause, effect, and significance are difficult to determine here, but it is interesting to draw a comparison between the lamellar organization of **1**·$2HSC_6H_4$-4-OH in the solid-state and the organization of lipid bilayers[28] and other surfacants[29] for which there is a natural preference for head-to-head and tail-to-tail organization.

In conclusion we note that hydrophilic and hydrophobic forces are often of the same magnitude as crystal packing forces.[30] The former are the same forces that give rise to aggregates of amphiphilic molecules in solution.[27-30] Although changing the properties of molecules of cocrystallization may not offer a

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(22) (a) Rao, C. N. R.; Gopalakrishnan, J. *New Directions in Solid State Chemistry*; Cambridge University Press: Cambridge, England, 1986; pp 351−359. (b) Day, P. In *Solid-State Chemistry*; Cheetham, A. K., Day, P., Eds.; Oxford Press: Oxford, England, 1992; Chapter 2, pp 31−59 and references therein. (c) See the series: *Physics and Chemistry of Materials with Layered Structures*; D. Reidel Publishing Co.: Dordrecht, The Netherlands.

(23) It should be once again emphasized that many molecular crystal structures can be *described* as low-dimensional, for example using the closest-packed approach of A. I. Kitaigorodsky (*Molecular Crystals and Molecules*, Academic Press: New York, 1973), but true low-dimensional solids should exhibit one or more physical properties that reflect their dimensionality.

(24) (a) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed; Oxford University Press: Oxford, England, 1984; pp 63−140. (b) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120 and references contained therein.

(25) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991, and references contained therein.

(26) Etter, M. C. *Acct. Chem. Res.* **1990**, *23*, 120.

(27) Ben-Naim, A. *Hydrophobic Interactions*; Plenum Press: New York, 1980.

(28) (a) Birdi, K. S. *Lipid and Biopolymer Monolayers at Liquid Interfaces*; Plenum Press: New York, 1989. (b) Bender, M., Ed.; *Interfacial Phenomena in Biological Systems*; Surfactant Science Series 39, Marcel Dekker: New York, 1991.

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general methodology for altering the dimensionality of crystalline materials, it is clear that the hydrophilic/hydrophobic properties of the molecules of cocrystallization S influence the dimensionality of the respective solid-state structures of the **1**·*n*Solv compounds described herein. Studies are underway to probe the physical properties of the lattices of **1**·$C_6H_6$ and **1**·$2HSC_6H_4$-4-OH. We also intend to investigate the properties of **1** in solution.

**Acknowledgment.** I am grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research (Grant 26002-G3) and to the University of Oklahoma Research Council for a Junior Faculty Summer Research Fellowship. The Petroleum Research Fund and University of Oklahoma Research Council contributed equally to defray publication costs.

**Supporting Information Available:** Tables of the crystallographic data, calculated coordinates of the hydrogen atoms, thermal parameters of the non-hydrogen atoms, and distances and angles of the bonded atoms of **1**·$C_6H_6$ and **1**·$2HSC_6H_4$-4-OH (4 pages). Ordering information is given on any current masthead page.

IC950071C