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## Synthesis, Structure, and Electronic Features of ( $\mu$ -Sulfido)bis[(*N,N'*-ethylenebis(salicylaldiminato))iron(III)], [Fe(salen)]<sub>2</sub>S, Containing the Only Authenticated Example of the Fe(III)–S–Fe(III) Single Bridge

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Received June 13, 1984

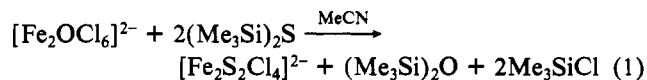
In a continuing investigation of sulfido-bridged iron complexes, the previously reported title compound was prepared by a new method, the reaction of [Fe(salen)]<sub>2</sub>O and (Me<sub>3</sub>Si)<sub>2</sub>S in dry DMF. [Fe(salen)]<sub>2</sub>S was obtained as a black solid that crystallizes in triclinic space group  $P\bar{1}$  with  $a = 10.792(2)$  Å,  $b = 11.746(2)$  Å,  $c = 13.215(3)$  Å,  $\alpha = 110.56(2)^\circ$ ,  $\beta = 99.23(2)^\circ$ ,  $\gamma = 72.27(2)^\circ$ , and  $Z = 2$ . With use of 2720 unique data ( $F_o^2 > 3\sigma(F_o^2)$ ) the structure was refined to  $R(R_w) = 4.33(4.48)$ . The molecule is binuclear with two [Fe(salen)]<sup>+</sup> half-dimers bridged by a sulfide atom. Ligands in the half-dimers are nonplanar and adopt the umbrella conformation; Fe–O and Fe–N bonds are of normal lengths. The Fe(III) atoms are displaced 0.591 and 0.625 Å from the least-squares N<sub>2</sub>O<sub>2</sub> coordination planes toward the  $\mu$ -S atom, forming pyramidal FeN<sub>2</sub>O<sub>2</sub>S units. The Fe–S–Fe bridge is unsymmetrical, with bond distances of 2.150(2) and 2.190(2) Å. The overall configuration of [Fe(salen)]<sub>2</sub>S is similar to that of its congeneric analogue [Fe(salen)]<sub>2</sub>O in its solvated and unsolvated crystalline forms. The Fe–S–Fe bridge angle of 121.8(1)° is substantially smaller than the Fe–O–Fe angle (145°) in [Fe(salen)]<sub>2</sub>O and any other binuclear Fe(III) complexes containing an unsupported  $\mu$ -oxo bridge. Magnetic susceptibility measurements at 22–291 K demonstrate that [Fe(salen)]<sub>2</sub>S is antiferromagnetic. Analysis of the data under the Hamiltonian  $\mathcal{H} = -JS_1 \cdot S_2$  provided an excellent fit with  $J = -176$  cm<sup>-1</sup> and  $g = 2.016$ . The most recent value for [Fe(salen)]<sub>2</sub>O is  $-178$  cm<sup>-1</sup>, showing essentially equal magnetic coupling of the two complexes when configured with the indicated bridge angles. A simple MO argument suggests that at equal bridge angles [Fe(salen)]<sub>2</sub>S may be the more strongly coupled. Isotropic <sup>1</sup>H NMR shifts are mainly contact in origin, and shift ratios with [Fe(salen)]<sub>2</sub>O indicate that hyperfine coupling constants at equivalent positions are different in the two complexes. In DMF solution [Fe(salen)]<sub>2</sub>S displays a S → Fe(III) charge-transfer band at 490 nm ( $\epsilon_M$  6930), similar to that of sulfide hemerythrin, and one-electron oxidation and reduction at  $-0.28$  and  $-1.27$  V vs. SCE, respectively. The reduction product has an oxidation level equivalent to that of the currently characterized state of sulfide hemerythrin. [Fe(salen)]<sub>2</sub>S is the only structurally authenticated example of a molecule with a Fe(III)–S–Fe(III) single bridge.

### Introduction

The bridge unit Fe(III)–O–Fe(III) is a frequent constituent of synthetic iron complexes.<sup>2</sup> It has been stabilized at 4-, 5-, and 6-coordinate Fe(III) sites, with prominent examples of the first two types being [Fe<sub>2</sub>OCl<sub>6</sub>]<sup>2-</sup><sup>3</sup> and [Fe(salen)]<sub>2</sub>O<sup>4-9</sup> and other complexes derived from salicylaldiminato ligands.<sup>7,10-13</sup> Complexes with unsupported bridges have varying Fe–O–Fe angles ( $\sim 140$ – $180^\circ$ <sup>3-6,10,11,14-16</sup>) and are invariably antiferromagnetic with  $-J \cong 180$ – $230$  cm<sup>-1</sup>.<sup>2,14,16</sup> This bridge is of biological significance as well. Its presence has been established in several met forms of the invertebrate oxygen-binding protein hemerythrin<sup>17</sup> (Hr) by X-ray diffraction<sup>17a,18</sup>

and EXAFS<sup>19</sup> investigations. Excellent models of the met-Hr active site have been prepared in which, as in the protein, the bridge is supported by two  $\mu$ -RCO<sub>2</sub><sup>-</sup> ligands.<sup>20,21</sup>

In contrast to the biological and extensive synthetic occurrence of the Fe<sub>2</sub>O unit, the supported or unsupported single-bridge Fe(III)–S–Fe(III) has not been structurally authenticated. This Fe<sub>2</sub>S unit poses a number of fundamental questions, including the value of the bridge angle and its variability and the transmission of electronic effects between half-dimers, compared to structurally analogous oxo-bridged complexes. Double bridges of this type have been shown to occur in, e.g., the extensively investigated antiferromagnetic dimers [Fe<sub>2</sub>( $\mu$ -S)<sub>2</sub>L<sub>4</sub>]<sup>2-</sup> (L = RS<sup>-</sup>, halide).<sup>22</sup> Corresponding oxo-bridged complexes are unknown. An attempt to prepare a singly bridged 4-coordinate dimer from [Fe<sub>2</sub>OCl<sub>6</sub>]<sup>2-</sup> and hexamethyldisilathiane, a reagent shown to be useful for O → S ligand substitution,<sup>23</sup> resulted in the formation of known [Fe<sub>2</sub>S<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup> in high yield in reaction 1.<sup>23a</sup> The only previously



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isolated compound possibly containing the desired bridge is  $[\text{Fe}(\text{salen})]_2\text{S}$ , which has been prepared by two different methods.<sup>8,24</sup> Its composition and antiferromagnetism<sup>8,25</sup> suggested that it is the sulfido analogue of  $[\text{Fe}(\text{salen})]_2\text{O}$ . However, a higher oligomeric form could not be eliminated, especially in view of a ligand flexibility sufficient to accommodate 6-coordinate structures with Fe(III)<sup>26</sup> and other metals.<sup>15,27,28</sup> Because of this possibility and our interest in  $\text{Fe}_2\text{S}$ -bridged complexes,<sup>22,29</sup>  $[\text{Fe}(\text{salen})]_2\text{S}$  has been synthesized by a new procedure, its structure determined by X-ray analysis, and certain of its electronic features examined.

### Experimental Section

**Preparation of  $[\text{Fe}(\text{salen})]_2\text{S}$ .** All operations were performed under a pure dinitrogen atmosphere. To a stirred slurry of 0.840 g (1.27 mmol) of  $[\text{Fe}(\text{salen})]_2\text{O}$ <sup>7</sup> (recrystallized from DMF/ether) in ~20 mL of DMF (dried over 3-Å molecular sieves) was added 0.31 mL (1.46 mmol) of  $(\text{Me}_2\text{Si})_2\text{S}$  (Petrarch Systems, Inc.). The mixture, which rapidly turned black, was stirred for 4 h. Anhydrous diethyl ether (~40 mL) was slowly added, and the mixture was cooled at 0 °C for several hours. The black microcrystalline solid was collected by filtration, washed extensively with ether, and dried in vacuo, affording 0.78 g of crude product. This material gave no evidence of the presence of  $[\text{Fe}(\text{salen})]_2\text{O}$  in its IR or <sup>1</sup>H NMR spectrum. DMF was detected in the <sup>1</sup>H NMR spectrum; it could not be removed under high vacuum ( $2 \times 10^{-6}$  torr, ~25 °C). A sample of 0.75 g of this solid was dissolved in ~150 mL of DMF, the solution was filtered, and ~300 mL of ether was layered on top of the filtrate. After 5 days, the mixture was filtered and the finely ground solid collected was washed thoroughly with ether and dried in vacuo ( $2 \times 10^{-6}$  torr, 24 h, ~25 °C). The product was obtained as black crystals (0.38 g (45%)), whose IR and <sup>1</sup>H NMR spectra indicated the absence of  $[\text{Fe}(\text{salen})]_2\text{O}$ . Anal. Calcd for  $\text{C}_{32}\text{H}_{28}\text{Fe}_2\text{N}_4\text{O}_4\text{S}$ : C, 56.83; H, 4.17; Fe, 16.51; N, 8.28; S, 4.74. Found: C, 56.66; H, 4.16; Fe, 17.21; N, 8.08; S, 4.66. The compound in solution is rapidly converted to  $[\text{Fe}(\text{salen})]_2\text{O}$  by traces of dioxygen and must be handled accordingly. The solid is stable for at least 1 day in air.

**Collection and Reduction of X-ray Data.** Black crystals of  $[\text{Fe}(\text{salen})]_2\text{S}$  were grown by diffusion of diethyl ether into a DMF solution at room temperature under strictly anaerobic and dry conditions. A needle-shaped crystal was lodged in a glass capillary and sealed under argon. Data were collected at room temperature (~24 °C) on a Nicolet R3m four-circle automated diffractometer by using graphite-monochromatized Mo K $\alpha$  radiation. The orientation matrix and unit cell dimensions were calculated by least-squares treatment of 25 machine-centered reflections ( $18^\circ \leq 2\theta \leq 30^\circ$ ). The data collection and crystal parameters are summarized in Table I. Three check reflections, measured every 60 reflections, exhibited no significant decay ( $\leq 3\%$ ) over the duration of data collection. The data were processed with the program XTAPE of the SHELXTL program package (Nicolet XRD Corp., Madison, WI). After equivalent reflections were merged,  $R_{\text{merge}}$  was ~4.3%. Empirical absorption corrections were applied by the program XEMP. Maximum and minimum transmission factors were 0.77 and 0.67. Extinction corrections were found to be insignificant and were not applied. The centric triclinic space group  $P\bar{1}$  was selected after analysis of intensities and axial photographs that revealed no diffraction symmetry higher than  $C_1$  ( $\bar{1}$ ). The space group was confirmed by successful solution and refinement of the structure.

**Solution and Refinement of the Structure.** The positions of the two iron atoms were located from Patterson maps. The direct-methods program SOLV confirmed the location of these atoms and indicated the position of the bridging sulfur atom. All remaining non-hydrogen atoms were located and their positional parameters refined by using difference Fourier techniques and blocked-cascade least-squares re-

Table I. Data Collection and Crystal Parameters for  $[\text{Fe}(\text{salen})]_2\text{S}$

formula (mol wt)	$\text{C}_{32}\text{H}_{28}\text{Fe}_2\text{N}_4\text{O}_4\text{S}$ (676.36)
<i>a</i> , Å	10.792 (2)
<i>b</i> , Å	11.746 (2)
<i>c</i> , Å	13.215 (3)
$\alpha$ , deg	110.56 (2)
$\beta$ , deg	99.23 (2)
$\gamma$ , deg	72.27 (2)
cryst syst	triclinic
<i>V</i> , Å <sup>3</sup>	1491.3 (6)
<i>Z</i>	2
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.50
<i>d</i> <sub>obsd</sub> , g/cm <sup>3</sup>	1.49 <sup>a</sup>
space group	$P\bar{1}$
cryst dims, mm	$0.28 \times 0.12 \times 0.18$
radiation ( $\lambda$ , Å)	Mo K $\alpha$ (0.710 69)
abs coeff ( $\mu$ ), cm <sup>-1</sup>	10.82
scan speed, deg/min	2.0–29.3 ( $\theta/2\theta$ scan)
$2\theta$ limits, deg	$4.0 \leq 2\theta \leq 45$
scan range, deg	$2.0 + (2\theta\text{K}\alpha_1 - 2\theta\text{K}\alpha_2)$
bkgd/scan time ratio	0.25
no. of data collcd	4391 reflns (+ <i>h</i> , ± <i>k</i> , ± <i>l</i> )
no. of unique data ( $F_o^2 > 3\sigma(F_o^2)$ )	2720
no. of variables	388
goodness of fit	1.56
<i>R</i> , %	4.33
<i>R</i> <sub>w</sub> , %	4.48

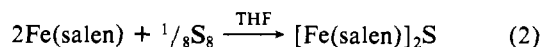
<sup>a</sup> Determined by the neutral buoyancy technique in  $\text{CCl}_4/n$ -hexane.

finement. Atomic scattering factors were taken from the tabulation of Cromer and Waber,<sup>30</sup> scattering factors were corrected for  $\Delta f'$  and  $i\Delta f''$  terms. Isotropic refinement of all non-hydrogen atoms converged at  $R = 8.9\%$ . All non-hydrogen atoms were then refined with anisotropic thermal parameters. In the last stages of refinement, hydrogen atoms with thermal parameters set at  $1.2\times$  that of the bonded carbon atom and the fixed C–H distance of 0.96 Å were included. The largest peak in a final difference Fourier map was  $0.48 \text{ e}/\text{\AA}^3$ . Unique data used in the refinement and final *R* values are given in Table I. Positional parameters of  $[\text{Fe}(\text{salen})]_2\text{S}$  are listed in Table II, and selected interatomic distances and angles are presented in Table III.<sup>31</sup>

**Other Physical Measurements.** Magnetic susceptibilities were measured at ~20–290 K with a Faraday balance equipped with an Oxford Instruments gas flow cryostat. The sample was loaded in the air, but during the experiment it was kept under 0.10 atm of He. Sulfur analysis after measurements were completed (4.71%) was consistent with no sample decomposition. The susceptibility of the sample at room temperature was independent of field in the 1–12-kG range, indicating the absence of ferromagnetic impurities. A diamagnetic correction of  $-423 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  was applied to the data. A tabulation of molar susceptibilities  $\chi_M$  at 99 points within the foregoing temperature range is available.<sup>31</sup> <sup>1</sup>H NMR spectra were measured at 300 MHz with use of a Bruker AM-300 spectrometer. Chemical shifts downfield of  $\text{Me}_4\text{Si}$  are designated as negative. Absorption spectra were obtained with a Cary Model 219 spectrophotometer. Cyclic voltammetry experiments were performed with standard PAR equipment at a 100 mV/s scan rate; a Pt working electrode and an aqueous SCE reference electrode were employed. DMF solutions contained 0.1 M (*n*-Bu<sub>4</sub>N)(ClO<sub>4</sub>) supporting electrolyte. All solution measurements were made in dry solvents under anaerobic conditions.

### Results and Discussion

**Synthesis of  $[\text{Fe}(\text{salen})]_2\text{S}$ .** This compound has been prepared by the addition of  $\text{Na}_2\text{S}$  to the filtrate from the formation of  $[\text{Fe}(\text{salen})]_2\text{O}$  from salicylaldehyde, ethylenediamine, and  $\text{FeSO}_4$  in methanol/water<sup>8</sup> and by the oxidative-addition reaction 2.<sup>24</sup> No yield was given for either procedure.



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Table II. Atom Coordinates ( $\times 10^4$ ) for [Fe(salen)]<sub>2</sub>S

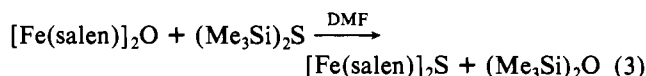
atom	x	y	z	atom	x	y	z
Fe(1)	6827 (1) <sup>a</sup>	9366 (1)	2907 (1)	C(21)	4279 (5)	9357 (5)	3668 (4)
Fe(2)	6295 (1)	6924 (1)	217 (1)	C(22)	4940 (5)	8251 (5)	4014 (4)
S	7317 (2)	8273 (1)	1231 (1)	C(23)	4156 (7)	7700 (6)	4348 (5)
O(1)	8220 (3)	10062 (3)	3691 (3)	C(24)	4739 (9)	6603 (7)	4615 (5)
O(2)	7086 (3)	8211 (3)	3707 (3)	C(25)	6054 (8)	6078 (6)	4573 (5)
O(3)	6717 (4)	6295 (4)	-1269 (3)	C(26)	6830 (6)	6618 (5)	4278 (4)
O(4)	4590 (4)	7837 (4)	-155 (3)	C(27)	6301 (5)	7722 (4)	3987 (4)
N(1)	6046 (4)	11066 (4)	2561 (3)	C(31)	8516 (5)	4494 (5)	-288 (4)
N(2)	4812 (4)	9868 (4)	3212 (3)	C(32)	8607 (5)	4537 (5)	-1359 (4)
N(3)	7674 (4)	5269 (4)	366 (3)	C(33)	9583 (5)	3600 (5)	-2012 (5)
N(4)	5354 (4)	6298 (4)	1129 (3)	C(34)	9666 (6)	3522 (6)	-3055 (5)
C(1)	4685 (5)	11182 (5)	2116 (4)	C(35)	8785 (7)	4380 (6)	-3484 (5)
C(2)	3997 (5)	10970 (5)	2918 (4)	C(36)	7819 (7)	5312 (6)	-2877 (5)
C(3)	7573 (7)	5104 (5)	1391 (4)	C(37)	7697 (6)	5420 (5)	-1800 (4)
C(4)	6164 (7)	5212 (5)	1460 (4)	C(41)	4198 (7)	6806 (6)	1433 (4)
C(11)	6611 (5)	11885 (4)	2642 (4)	C(42)	3271 (6)	7860 (5)	1139 (4)
C(12)	7944 (6)	11847 (4)	3118 (4)	C(43)	2064 (7)	8432 (7)	1648 (5)
C(13)	8514 (6)	12770 (5)	3080 (5)	C(44)	1170 (7)	9436 (7)	1427 (6)
C(14)	9723 (7)	12821 (6)	3532 (5)	C(45)	1440 (7)	9935 (7)	698 (6)
C(15)	10434 (6)	11956 (6)	4053 (4)	C(46)	2584 (6)	9385 (6)	166 (5)
C(16)	9909 (6)	11043 (5)	4098 (4)	C(47)	3522 (5)	8334 (5)	384 (4)
C(17)	8670 (5)	10959 (4)	3627 (4)				

<sup>a</sup> Estimated standard deviation in least significant figure given in parentheses in this and other tables.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for [Fe(salen)]<sub>2</sub>S

Fe(1)-S	2.190 (2)	Fe(2)-S	2.150 (2)
Fe(1)-O(1)	1.912 (4)	Fe(2)-O(3)	1.916 (4)
Fe(2)-O(2)	1.929 (4)	Fe(2)-O(4)	1.912 (4)
Fe(1)-N(1)	2.097 (4)	Fe(2)-N(3)	2.108 (4)
Fe(1)-N(2)	2.138 (4)	Fe(2)-N(4)	2.120 (4)
Fe...Fe	3.792		
O(1)-C(17)	1.320 (8)	O(3)-C(37)	1.318 (6)
O(2)-C(27)	1.315 (8)	O(4)-C(47)	1.319 (7)
N(1)-C(1)	1.476 (7)	N(3)-C(3)	1.459 (8)
N(2)-C(2)	1.467 (7)	N(4)-C(4)	1.475 (7)
N(1)-C(11)	1.254 (8)	N(3)-C(31)	1.263 (6)
N(2)-C(21)	1.276 (9)	N(4)-C(41)	1.271 (8)
C(1)-C(2)	1.512 (10)	C(3)-C(4)	1.502 (10)
S-Fe(1)-O(1)	110.3 (1)	S-Fe(2)-O(3)	113.4 (2)
S-Fe(1)-O(2)	108.6 (1)	S-Fe(2)-O(4)	107.9 (1)
S-Fe(1)-N(1)	93.2 (1)	S-Fe(2)-N(3)	98.4 (1)
S-Fe(1)-N(2)	115.6 (1)	S-Fe(2)-N(4)	112.2 (1)
O(1)-Fe(1)-O(2)	94.0 (2)	O(3)-Fe(2)-O(4)	90.5 (2)
O(1)-Fe(1)-N(1)	86.4 (2)	O(3)-Fe(2)-N(3)	85.9 (2)
O(2)-Fe(1)-N(2)	85.9 (2)	O(4)-Fe(2)-N(4)	86.3 (2)
N(1)-Fe(1)-N(2)	76.4 (2)	N(3)-Fe(2)-N(4)	76.5 (2)
Fe(1)-S-Fe(2)	121.8 (1)		

Product analytical data were,<sup>8</sup> or were described<sup>24</sup> as, satisfactory. In this work, [Fe(salen)]<sub>2</sub>S was prepared by reaction 3 in *dry* DMF. Hexamethyldisiloxane was identified as the



other reaction product by <sup>1</sup>H NMR spectroscopy. The pure product was obtained in 45% yield after recrystallization from DMF/ether as black crystals slightly soluble in most common polar organic solvents. Exposure of solutions to trace quantities of dioxygen results in immediate conversion to [Fe(salen)]<sub>2</sub>O. The occurrence of reaction 3 further underscores the utility of hexamethyldisilathiane as an O → S ligand substitution reagent. Although there now exist a number of examples of terminal O → S atom substitution with this reagent,<sup>23,32</sup> reaction 3 is the first case of a one-for-one bridge atom substitution. Reaction 1 presumably does not take a similar course

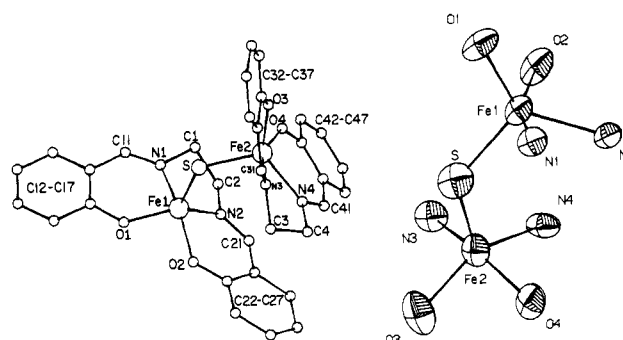


Figure 1. Structure of [Fe(salen)]<sub>2</sub>S: left, entire structure and atom-labeling scheme; right, structures of the coordination spheres with 50% probability ellipsoids shown.

because of labile chloride ligands in [Fe<sub>2</sub>OCl<sub>6</sub>]<sup>2-</sup>.

**Description of the Structure.** The depiction in Figure 1 immediately reveals that [Fe(salen)]<sub>2</sub>S is a binuclear molecule with a single  $\mu$ -S bridge and thus has an overall structure similar to that of [Fe(salen)]<sub>2</sub>O in its solvated<sup>4,5</sup> and unsolvated<sup>6</sup> crystalline forms. The asymmetric unit contains one molecule with no imposed symmetry; each half-dimer exhibits small structural differences. Selected interatomic distances and angles are set out in Table III. The bridge unit is asymmetric, the Fe-S distances being 2.150 (2) and 2.190 (2) Å. These are ca. 0.37 Å longer than the Fe-O bridge bonds in [Fe(salen)]<sub>2</sub>O<sup>4-6</sup> and [Fe(R-N-sal)]<sub>2</sub>O complexes.<sup>10,11</sup> The displacements of the iron atoms from the best least-squares planes through the appropriate N<sub>2</sub>O<sub>2</sub> unit toward the bridging sulfur atom are 0.591 Å (Fe(1)) and 0.625 Å (Fe(2)). The Fe...Fe distance of 3.792 Å precludes direct metal-metal interaction. Values of Fe-O and Fe-N bond distances are unexceptional compared to those of related molecules.<sup>4-6,10,11</sup>

As is the case for [Fe(salen)]<sub>2</sub>O,<sup>6</sup> its dichloromethane<sup>5</sup> and bis(pyridine)<sup>4</sup> solvates, and monomeric Fe(salen)Cl,<sup>33</sup> the two salen ligands of [Fe(salen)]<sub>2</sub>S adopt the asymmetric "umbrella" conformation. The two salicylaldehyde portions of one ligand are folded back along the N-O line of each chelate ring from those in the other half-dimer. In terms of the dihedral angle convention of Calligaris et al.,<sup>15</sup>  $\gamma \cong \alpha + \beta$ . These angles are defined in Table IV, whose data show that

(32) Minelli, M.; Enemark, J. H.; Wieghardt, K.; Hahn, M. *Inorg. Chem.* 1983, 22, 3952.

(33) Gerloch, M.; Mabbs, F. E. *J. Chem. Soc. A* 1967, 1598.

Table IV. Structural Data for  $[\text{Fe}(\text{salen})]_2\text{X}$  (X = O, S)

compd	Fe-X, <sup>a</sup> Å	X-Fe-X, deg	<i>d</i> , <sup>b</sup> Å	$\alpha$ , <sup>c</sup> deg	$\beta$ , <sup>c</sup> deg	$\gamma$ , <sup>d</sup> deg	ref
[Fe(salen)] <sub>2</sub> S	2.170	121.8 (1)	0.591	12.0	17.4	29.4	this work
			0.625	11.5	17.2	26.6	
[Fe(salen)] <sub>2</sub> O	1.78	144.6 (6)	0.581	4.5	14.3	10.7	6
			0.572	2.5	15.0	16.2	
[Fe(salen)] <sub>2</sub> O·2py	1.797	139.1 (9)	0.570	19.7	21.4	41.0	4
[Fe(salen)] <sub>2</sub> O·CH <sub>2</sub> Cl <sub>2</sub>	1.794	142.2	0.549	9.9	15.8	24.1	5
			0.570	11.3	23.6	34.3	
			0.550	11.9	14.7	26.4	

<sup>a</sup> Mean value. <sup>b</sup> Displacement of Fe atom from N<sub>2</sub>O<sub>2</sub> least-squares plane. <sup>c</sup> Dihedral angle between O<sub>2</sub>N<sub>2</sub> coordination plane and least-squares planes of salicylaldiminato groups. <sup>d</sup> Dihedral angle between salicylaldiminato group planes.

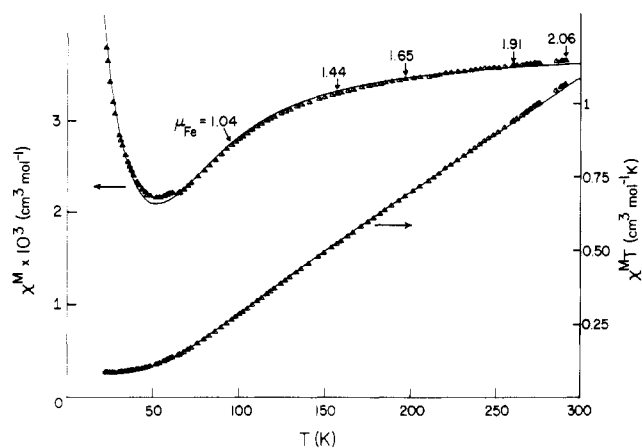
these angular measures of ligand nonplanarity in  $[\text{Fe}(\text{salen})]_2\text{S}$  are within the range of values for the  $\mu$ -oxo structures. Displacements of Fe(III) atoms from the two coordination planes tend to be larger. The most interesting structural aspect of  $[\text{Fe}(\text{salen})]_2\text{S}$  is the bridge angle of 121.8 (1)°. Given the general tendency of sulfur to form smaller angles than oxygen, it is perhaps not surprising that this angle is less than that in  $[\text{Fe}(\text{salen})]_2\text{O}$ , which is subject to small variations in different crystal lattices. Compared to unsolvated  $[\text{Fe}(\text{salen})]_2\text{O}$ , the difference in angles is quite appreciable (23°). Further, the Fe-S-Fe angle is smaller than any reported Fe-O-Fe angle of an unsupported bridge. Only in the hemerythrin site models  $\text{Fe}_2\text{O}(\text{HB}(\text{pz})_3)_2(\text{OAc})_2$ <sup>20</sup> (123.5 (1)°) and  $[\text{Fe}_2\text{O}(\text{C}_8\text{H}_{20}\text{N}_4)_2(\text{OAc})_2]^{2+21}$  (118.3 (5)°), containing supported Fe<sub>2</sub>O bridges, are comparable or smaller bridge angles found. These angles are presumably constrained by the acetate bridges. Assessment of the sensitivity of the Fe<sub>2</sub>S bridge angle to lattice effects and steric interactions between half-dimers requires synthesis of appropriately substituted complexes and additional structure determinations.

**Magnetism.** The magnetic behavior of  $[\text{Fe}(\text{salen})]_2\text{S}$  has been examined earlier by Mitchell and Parker<sup>8</sup> at 11 temperatures in the 99–293 K range. In this work the magnetic susceptibility of a polycrystalline sample prepared by reaction 3 was determined at 22.0–290.5 K. The results, plotted as  $\chi_M$  and  $\chi_M T$  vs. *T*, are provided in Figure 2. Values of  $\chi_M$  decrease slowly from the highest temperature of measurement to ~50 K, where they increase owing to the presence of a paramagnetic impurity. This impurity is also responsible for the flat region of the  $\chi_M T$  curve below 50 K. Values of the magnetic moment per Fe atom ( $\mu_{\text{Fe}}$ ) are well below the Curie value for  $S = 5/2$  Fe(III). The shapes of both curves are characteristic of strong antiferromagnetic coupling and resemble the behavior of  $[\text{Fe}(\text{salen})]_2\text{O}$ , where paramagnetic impurities are also found at low temperature.<sup>9</sup> Under the usual spin Hamiltonian  $\mathcal{H} = -JS_1 \cdot S_2$ , the energy levels are readily obtained and the magnetic susceptibility is given by eq 4, in

$$\chi_M = (g^2 \beta^2 N / 3kT) \left\{ \sum_{S=0}^5 (2S+1)S(S+1) \times \exp[-JS(S+1)/2kT] \right\} / \left\{ \sum_{S=0}^5 (2S+1) \times \exp[-JS(S+1)/2kT] \right\} (1-\rho) + (35\beta^2 N / 3kT)\rho \quad (4)$$

which  $\rho$  is the fraction of paramagnetic impurity, taken as high-spin Fe(III), and the other symbols have their usual meanings. An excellent simulation of the experimental results is obtained with  $J = -176 \text{ cm}^{-1}$ ,  $g = 2.013$ , and  $\rho = 1.98 \times 10^{-2}$ , corresponding to an agreement factor  $R = 1.30 \times 10^{-4}$ .

Mitchell and Parker<sup>8</sup> have reported the value  $J = -150 \text{ cm}^{-1}$  for  $[\text{Fe}(\text{salen})]_2\text{S}$ , derived from a less extensive magnetic data



**Figure 2.** Temperature dependence of the molar magnetic susceptibility  $\chi_M$  and  $\chi_M T$  of polycrystalline  $[\text{Fe}(\text{salen})]_2\text{S}$ . The horizontal arrows indicate the appropriate ordinate. Solid lines are fits to the data using eq 4 and the parameters in the text. Magnetic moments per Fe atom  $\mu_{\text{Fe}} = 2.828(\chi_M T)^{1/2}$  are given at 98.0, 157.2, 196.8, 254.8, and 290.5 K. Results of Mitchell and Parker<sup>8</sup> at these temperatures ( $\pm 2$  K) are  $\mu_{\text{Fe}} = 1.27, 1.64, 1.82, 2.09,$  and  $2.23 \mu_B$ .

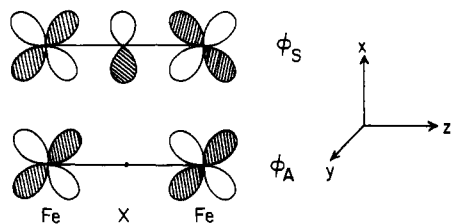
set. Our value of  $-176 \text{ cm}^{-1}$  is indicative of stronger coupling. At ambient temperature, where impurity corrections should be negligible, we find  $\mu_{\text{Fe}} = 2.06 \mu_B$  (290 K), compared to the earlier values of  $2.16 \mu_B$  (295 K)<sup>8</sup> and  $2.23 \mu_B$  (293 K).<sup>24</sup> Comparisons at other temperatures are given in Figure 2. Exchange coupling constants for  $[\text{Fe}(\text{salen})]_2\text{O}$  and related Schiff base complexes occur in the ca.  $-170$  to  $-200 \text{ cm}^{-1}$  range.<sup>2,7-9,13,35</sup> The latest value for  $[\text{Fe}(\text{salen})]_2\text{O}$  is  $-178 \text{ cm}^{-1}$ .<sup>9</sup> This is presumably the most reliable determination of  $J$  for this complex inasmuch as it includes a fit of susceptibility data over the widest temperature range. Therefore, we conclude that  $[\text{Fe}(\text{salen})]_2\text{O}$  (145°) and  $[\text{Fe}(\text{salen})]_2\text{S}$  (122°) are essentially equally magnetically coupled when configured with the indicated bridge angles.<sup>36</sup> Because of the difference in bridge angles, the experimental results do not provide an immediate answer to the important issue as to which bridge atom, oxo or sulfido, is the inherently better mediator of exchange coupling. The variation of  $J$  with bridge angle has been studied theoretically by Hay et al.<sup>37</sup> Certain of their results can be expressed as eq 5, similar in form to an equation derived earlier

$$J = (-1/n^2) \sum_{i=1}^n \Delta_i^2 / U_i + (2/n^2) \sum_{i,j} K_{ij} \quad (5)$$

- (35) Jezowska-Trzebiatowska, B.; Kozłowski, H.; Cukierda, T.; Ozarowski, A. *J. Mol. Struct.* **1973**, *19*, 663.
- (36) This statement assumes that the crystallographic<sup>6</sup> and magnetic<sup>9</sup> samples of  $[\text{Fe}(\text{salen})]_2\text{O}$ , reportedly prepared in the unsolvated condition by different methods, are the same. However, the difference in  $J$  values for this complex and its  $\text{CH}_2\text{Cl}_2$  adduct, taken from the same study,<sup>7</sup> is <10%. Thus, small variations in bridge angle (Table IV) produce small but apparently determinable differences in  $J$ .
- (37) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

(34)  $R = \sum [\chi_M(\text{exptl}) - \chi_M(\text{calcd})]^2 / \sum [\chi_M(\text{exptl})]^2$ . A fit nearly as good is obtained with  $J = -181 \text{ cm}^{-1}$ ,  $g = 2.049$ , and  $\rho = 2.00 \times 10^{-2}$  ( $R = 1.68 \times 10^{-4}$ ). In the discussion we retain the parameters in the text inasmuch as they include a  $g$  value nearer to 2, as expected for high-spin Fe(III).

by Anderson,<sup>38</sup> for a symmetric dimer containing centers A and B, each of which has  $n$  unpaired electrons. Here  $U_i$  is an interelectron repulsion parameter on A and B,  $K_{ij}$  is the positive exchange integral between magnetic orbitals  $d_i^A$  and  $d_j^B$ , and  $\Delta_i = 2|\beta_i|$  is the energy separation of the MO's formed from  $d_i^A$  and  $d_i^B$ . The second term (ferromagnetic contribution) is normally taken as less sensitive<sup>37</sup> to the structural and electronic perturbations that affect the antiferromagnetic interactions, described by the first term. From previous analyses in the MO framework,<sup>37,39</sup> the origin of the variation of  $J$  in the high-spin  $d^5$ - $d^5$  case is mainly due to variation in the energy separation of MO's  $\phi_A$  and  $\phi_S$  formed from  $d_{xz}^A$  and  $d_{xz}^B$ . When the bridge angle closes, the energy of  $\phi_A$  increases slightly and that of  $\phi_S$  decreases.<sup>39</sup> Thus, the gap  $\Delta_{xz}$  decreases, and from eq 5, this should result in a decrease in  $|J|$ . It follows that, because [Fe(salen)]<sub>2</sub>S with a smaller bridge angle has the same  $J$  value as [Fe(salen)]<sub>2</sub>O, the former should be the more strongly coupled at equal bridge angles.



The prediction from this simple qualitative argument, viz., that at parity of terminal ligands, coordination geometry, and bridge angle, a sulfido bridge is a better mediator of antiferromagnetic interactions than an oxo bridge, requires an experimental test. We suspect that the bridge angle in [Fe(salen)]<sub>2</sub>S is essentially a minimum value and that, as with the oxo-bridged complexes,<sup>4-6,10,11</sup> this angle is set by ligand conformations and intradimer steric interactions. Manipulation of these factors in a manner already accomplished for the oxo complexes<sup>10-13</sup> should lead to larger Fe-S-Fe angles and a suitable test of the preceding statement.<sup>40</sup>

**Other Properties.** Certain comparative properties of [Fe(salen)]<sub>2</sub>S and [Fe(salen)]<sub>2</sub>O have been examined. <sup>1</sup>H NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> solutions at 296 K are set out in Figure 3. The isotropic shifts of [Fe(salen)]<sub>2</sub>O<sup>41</sup> have been shown to be predominantly contact in origin.<sup>42</sup> The alternating signs of ring proton shifts indicate that this property also applies to [Fe(salen)]<sub>2</sub>S.<sup>41</sup> If the shifts are purely contact, the ratio of shifts of corresponding nuclei  $i$  in two molecules (S, O) is given by eq 6<sup>43</sup> at fixed temperature. This relation has not been

$$\left(\frac{\Delta H}{H_0}\right)_{\text{con,S}} / \left(\frac{\Delta H}{H_0}\right)_{\text{con,O}} = A_{i,S} X_{M,S} / A_{i,O} X_{M,O} \quad (6)$$

tested by measurement of solution susceptibilities because of

(38) Anderson, P. W. In "Magnetism"; Rado, G. T., Suhl, H., Eds.; Academic Press: New York, 1963.

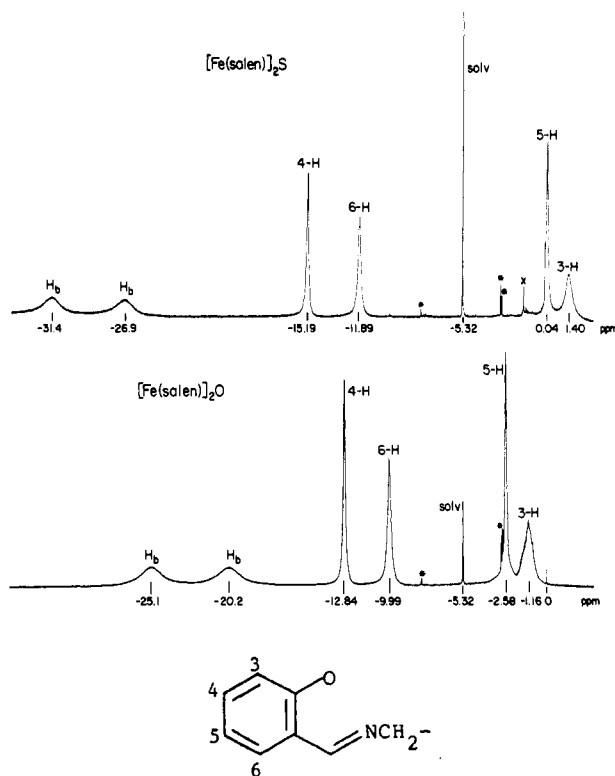
(39) Tatsumi, K.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 3328.

(40) In this connection it is noted that there is no clear experimental verification, with iron(III) salicylaldiminato compounds, of the expectation that increasing the Fe-O-Fe angle increases the  $J$  value. The  $\sim 30^\circ$  increase in angle upon passing from [Fe(salen)]<sub>2</sub>O<sup>6</sup> ( $-J = 178-190 \text{ cm}^{-1}$ <sup>7-9,35</sup>) to [Fe(*p*-ClC<sub>6</sub>H<sub>4</sub>-sal)]<sub>2</sub>O<sup>11</sup> ( $-J = 200 \pm 32 \text{ cm}^{-1}$ <sup>13</sup>) is nearly the largest change between any two members of the set, but the  $J$  values, especially from earlier susceptibility data at  $\sim 80 \text{ K}$  and higher,<sup>7,8,13</sup> are not sufficiently precise to reflect a trend.

(41) <sup>1</sup>H-NMR (ppm) of [Fe(salen)]<sub>2</sub>S ([Fe(salen)]<sub>2</sub>O): 3-H, +8.29 (+5.73); 4-H, -7.94 (-5.59); 5-H, +6.87 (+4.25); 6-H, -4.68 (-2.78); H<sub>b</sub>, -23.1, -27.6 (-16.4, -21.3).  $(\Delta H/H_0)_{\text{iso}} = (\Delta H/H_0)_{\text{obsd}} - (\Delta H/H_0)_{\text{dia}} (\text{H}_2\text{salen})$ .

(42) La Mar, G. N.; Eaton, G. R.; Holm, R. H.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 63.

(43) Reynolds, J. G.; Laskowski, E. J.; Holm, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 5315.



**Figure 3.** <sup>1</sup>H NMR spectra (300 MHz, 296 K) of [Fe(salen)]<sub>2</sub>S and [Fe(salen)]<sub>2</sub>O in CD<sub>2</sub>Cl<sub>2</sub> solutions. Signal assignments are indicated. Key: solv = solvent; x = impurity; asterisk indicates residual DMF.

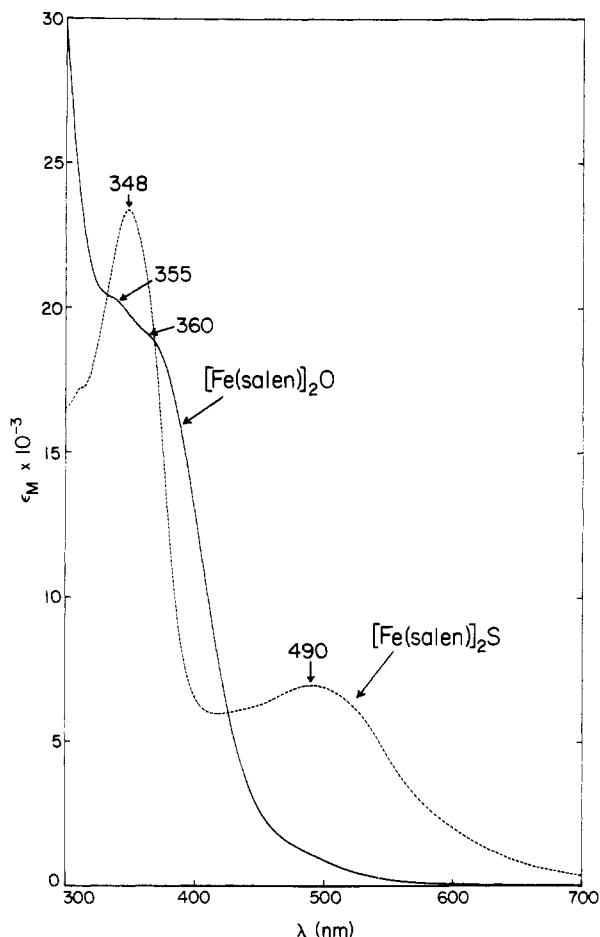
the low solubility of the complexes, especially over the appreciable temperature interval required.<sup>42</sup> However, the varying isotropic shift ratios<sup>41</sup> of 1.30-1.68 are indicative of differences in electron-proton hyperfine coupling constants  $A_i$  in the two molecules. This assumes that any dipolar contributions from the zero-field splitting of high-spin Fe(III)<sup>42</sup> are minor. Any further analysis of the isotropic shifts will require preparation and magnetic measurements of an adequately soluble derivative of [Fe(salen)]<sub>2</sub>S, as has been done for [Fe(salen)]<sub>2</sub>O.<sup>42</sup> In this connection it is noted that bridge angles in the solid state are not necessarily preserved in solution. For example, in chloroform solution  $\mu_{\text{Fe}} = 1.3 \mu_{\text{B}}$  for [Fe(*n*-Pr-sal)]<sub>2</sub>O at ambient temperature, whereas in the solid state the value is  $1.86 \mu_{\text{B}}$ .<sup>44</sup> From the foregoing discussion of magnetic coupling, this result suggests an increase over the solid-state Fe-O-Fe angle of  $164(5)^\circ$ <sup>10</sup> and, therewith, of the  $J$  value of ca.  $-200 \text{ cm}^{-1}$ .<sup>13,40</sup>

The comparative absorption spectra in Figure 4 reveal a strong visible band at 490 nm ( $\epsilon_{\text{M}} 6930$ ) for [Fe(salen)]<sub>2</sub>S in DMF solution. This feature is assigned to S  $\rightarrow$  Fe(III) charge transfer inasmuch as [Fe(salen)]<sub>2</sub>O lacks strong absorption in this region. This spectrum finds close analogy with that of a species generated in aqueous solution and formulated as [Fe(HEDTA)]<sub>2</sub>S<sup>2-</sup>, for which  $\lambda_{\text{max}} (\epsilon_{\text{M}}) = 490 (\sim 8900) \text{ nm}$ .<sup>45</sup> Its oxo-bridged analogues exhibit only weak visible absorption ( $\epsilon_{\text{M}} \lesssim 100$ ).<sup>46</sup> The higher energy bands in Figure 3 presumably arise from ArO<sup>-</sup>  $\rightarrow$  Fe(III) charge transfer. The solution spectrum of [Fe(salen)]<sub>2</sub>S is in fair agreement with data tabulated for the solid,<sup>8</sup> except for the lack of a discrete feature near 380 nm.

(44) Boyd, P. D. W.; Murray, K. S. *J. Chem. Soc. A* **1971**, 2711.

(45) Philip, C. V.; Brooks, D. W. *Inorg. Chem.* **1974**, *13*, 384. (HEDTA = *N*-(hydroxyethyl)ethylenediaminetriacetate).

(46) Schugar, H. J.; Hubbard, A. T.; Anson, F. C.; Gray, H. B. *J. Am. Chem. Soc.* **1969**, *91*, 71. Schugar, H. J.; Rossman, G. R.; Barraclough, C. G.; Gray, H. B. *Ibid.* **1972**, *94*, 2683.



**Figure 4.** Absorption spectra of  $[\text{Fe}(\text{salen})]_2\text{S}$  and  $[\text{Fe}(\text{salen})]_2\text{O}$  in DMF solutions in the UV-visible region.  $[\lambda_{\text{max}}, \text{nm} (\epsilon_M)]: 490 (6930), 348 (23\,500); 360 (19\,200), 355 (20\,400)$ .

**Possible Biological Relevance.** Aquomet-Hr and  $\text{H}_2\text{S}$  or sulfide at  $\text{pH} \sim 8$  form a species, sulfide-Hr, with the composition  $2 \text{Fe}:\text{S}^{2-}$ .<sup>47,48</sup> Sulfide-Hr is a chromophore with a band at 510 nm ( $\epsilon_M \sim 1200$ ), suggesting, as previously recognized,<sup>47</sup> a relationship with  $[\text{Fe}(\text{salen})]_2\text{S}$  and  $[\text{Fe}(\text{HEDTA})]_2\text{S}^{2-}$ .

Recent work<sup>48</sup> has shown that sulfide-Hr is stabilized in the mixed-valence  $\text{Fe}(\text{III}) (S = 5/2) + \text{Fe}(\text{II}) (S = 2)$  oxidation level, which is spin coupled to give a  $S = 1/2$  ground state. Valence states are trapped on the Mössbauer time scale. Consequently, the  $\text{Fe}_2\text{S}$  portions of sulfide-Hr and  $[\text{Fe}(\text{salen})]_2\text{S}$  are not isoelectronic. However, in DMF solution  $[\text{Fe}(\text{salen})]_2\text{S}$  undergoes a well-defined electrochemical reduction at  $E_{1/2} = -1.27 \text{ V vs. SCE}$  ( $\Delta E_p = 80 \text{ mV}$ ,  $i_{p,c}/i_{p,a} \cong 1$ ). The corresponding reduction of  $[\text{Fe}(\text{salen})]_2\text{O}$  in DMF occurs at  $-1.07 \text{ V}$ . In  $\text{Me}_2\text{SO}$  solution the potential is  $-1.05 \text{ V}$ .<sup>49</sup>  $[\text{Fe}(\text{salen})]_2\text{S}$  also exhibits a one-electron oxidation in DMF at  $-0.28 \text{ mV}$  ( $\Delta E_p = 90 \text{ mV}$ ,  $i_{p,c}/i_{p,a} \cong 1$ ).  $[\text{Fe}(\text{salen})]_2\text{O}$  is reported to afford only poorly resolved electrochemical oxidation, but its diiron(III,IV) level has been reached by chemical oxidation and isolated.<sup>9</sup> These observations raise the possibility of isolating or generating the species  $[\text{Fe}(\text{salen})]_2\text{S}^{+}$ , with the anion being isoelectronic with the currently characterized state of sulfide-Hr. For the latter, available evidence does not permit a distinction between the proposed<sup>47</sup> structures  $\text{Fe}-\text{S}^{2-}-\text{Fe}$  and  $\text{Fe}\cdots\text{Fe}-\text{S}^{2-}$ . Such a distinction may be possible upon elucidation of the properties of  $[\text{Fe}(\text{salen})]_2\text{S}$ .

In summary, this research provides characterization of the only structurally authenticated example of the  $\text{Fe}(\text{III})-\text{S}-\text{Fe}(\text{III})$  single bridge. The set  $[\text{Fe}(\text{salen})]_2\text{S}^{-0,+}$  (stability permitting) provides an attractive opportunity for further study of structural and electronic properties mediated by a sulfide bridge, including trapped vs. delocalized valence states and magnetic coupling.

**Acknowledgment.** This research was supported by NIH Grant GM 28856. NMR and X-ray diffraction equipment were obtained by NSF Grants CHE 80-00670 and CHE 80-08891.

**Supplementary Material Available:** Listings of anisotropic temperature factors, calculated hydrogen atom positions, magnetic susceptibility data (22–291 K), and observed and calculated structure factors for  $[\text{Fe}(\text{salen})]_2\text{S}$  (21 pages). Ordering information is given on any current masthead page.

(47) Freier, S. M.; Duff, L. L.; Van Duyne, R. P.; Klotz, I. M. *Biochemistry* **1979**, *18*, 5372.

(48) Kurtz, D. M., Jr.; Sage, J. T.; Hendrich, M.; Debrunner, P. G.; Lukat, G. S. *J. Biol. Chem.* **1983**, *258*, 2115.

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## Linear Polysiloxanes from Dichlorosilane

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Received June 19, 1984

Polysiloxanes of type  $\text{RR}'\text{R}''\text{SiO}(\text{SiH}_2\text{O})_n\text{SiRR}'\text{R}''$  ( $\text{R}, \text{R}', \text{R}'' = \text{Me}, \text{Me}, \text{Me}; \text{Me}, \text{H}, \text{H}; \text{Et}, \text{Et}, \text{Et}; \text{Me}, \text{Me}, \text{H}$ ) have been prepared by three different methods: (1) reactions of  $\text{ClSiH}_2\text{O}(\text{SiH}_2\text{O})_n\text{SiH}_2\text{Cl}$  with  $\text{CH}_3\text{MgBr}$ ,  $\text{Me}_3\text{SiOH}$ , and  $\text{Et}_3\text{SiOH}$ ; (2)  $\text{H}_2\text{SO}_4$ -catalyzed equilibration of cyclic  $[\text{H}_2\text{SiO}]_n$  oligomers with  $\text{Me}_3\text{SiOSiMe}_3$ ; (3) cohydrolysis of  $\text{H}_2\text{SiCl}_2$  with  $\text{Me}_3\text{SiCl}$  and  $\text{Me}_2\text{HSiCl}$  using  $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ -buffered media. Lower species,  $\text{Me}_2\text{RSiO}(\text{SiH}_2\text{O})_n\text{SiMe}_2\text{R}$  ( $n = 1-3$ ), were isolated and characterized ( $\text{R} = \text{Me}, \text{H}$ ).

### Introduction

In an earlier paper<sup>2</sup> we described the cyclic polysiloxanes,  $[\text{H}_2\text{SiO}]_n$ , which are obtained when dichlorosilane,  $\text{H}_2\text{SiCl}_2$ , is hydrolyzed under the appropriate conditions.<sup>3</sup> Also of

interest to us were linear siloxanes of the type  $\text{RR}'\text{R}''\text{SiO}[\text{SiH}_2\text{O}]_n\text{SiRR}'\text{R}''$ , where  $\text{R}, \text{R}'$ , and  $\text{R}''$  can be the same or different. We report here our studies directed toward this goal. Linear polysiloxanes containing  $\text{H}_2\text{SiO}$  units in the polysiloxane chain have been reported in the patent literature.

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(2) Seyferth, D.; Prud'homme, C. C.; Wiseman, G. H. *Inorg. Chem.* **1983**, *22*, 2163.

(3) Previous studies of the hydrolysis of dichlorosilane are discussed in ref 2.