metry of the molecule is $C_{2h}$, only two Pd–allyl stretching bands are infrared active. These two bands can be designated as the antisymmetric and symmetric Pd–allyl stretching modes. Alternatively, they can be called the ring-tilt and metal–ring stretching modes,[15] respectively, if the allyl group is regarded as a semi-ring.

It should be noted that bonding scheme B involving only one valence bond may also exhibit the ring-tilt and metal–ring stretching modes. In this case, however, the ring-tilt frequency is expected to be much lower than the metal–ring stretching frequency because the former mode is regarded as a pure bending vibration involving the change in the angle between the valence bond and the allyl plane. Our infrared study seems to favor bonding scheme A since the frequencies of two Pd–allyl vibrations are relatively close (*ca.* 400 and 370 $cm^{-1}$).

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# Sulfur-Bridged Dimeric Complexes of Iron(III)

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**Abstract:** Iron(III) dimers of general formula $[Fe(S_2CSR)_2(SR)]_2$, R = $C_2H_5$, $n$-$C_3H_7$, $n$-$C_4H_9$, $C_6H_5CH_2$, have been synthesized. Under identical conditions, only the known monomeric compound $[Fe(S_2CSR)_3]$ has been isolated for R = $t$-$C_4H_9$. Molecular weight and proton nmr spectral studies of the diamagnetic dimers in solution have been carried out. The pmr spectrum of the ethyl dimer, assigned on the basis of spin-decoupling experiments, is consistent with a structure which contains bridging ethyl sulfide and both bridging and terminal ethyl thioxanthate ligands. Cyclic voltammetric and conventional polarographic studies of the metal–metal bonded dimers reveal a two-electron reduction wave and a one-electron oxidation wave, both irreversible. Tris($t$-butylthioxanthato)iron(III) is monomeric in solution and exhibits reversible one-electron oxidation and one-electron reduction waves. The complex contains low-spin iron(III) with an effective moment of 2.46 BM at room temperature in the solid and over the limited temperature range, $210° < T < 293°K$, in dichloromethane solution. The solid-state reflectance and solution electronic spectra of all the dimers are nearly identical, implying similar structures, but differ significantly from the corresponding spectra of the $t$-butyl monomer. Infrared spectra are reported and discussed.

Sulfur-bridged dimers of iron in low formal oxidation states have been prepared[2–5] and structurally characterized.[6–8] In addition, several dimeric 1,2-dithiolene complexes of iron in formally higher oxidation states have been synthesized,[9] and the solid-state structure of at least one member of this series has been determined.[10] An objective in a continuing study[11–13] of the coordination chemistry of iron–sulfur complexes of possible relevance to certain non-heme iron protein systems has been to synthesize iron(III) dimers or oligomers with bridging sulfide or alkyl mercaptide ligands. As reported in a preliminary communication,[13] this has been accomplished for one system by means of the carbon disulfide elimination reaction of iron(III) alkylthioxanthate complexes.

Carbon disulfide elimination reactions appear to be characteristic of metal thioxanthate complexes.[14] For example, it has recently been shown[15] that $Ni(S_2CSR)_2$ complexes may be decomposed, with loss of carbon disulfide, to the dimeric species $[Ni(S_2CSR)(SR)]_2$ reported earlier.[16] A similar reaction occurs in the thermal conversion of monomeric $[(\pi\text{-}C_5H_5)Fe(CO)(S_2CSR)]$ compounds to $[(\pi\text{-}C_5H_5)Fe(CO)(SR)]_2$.[4] Tris(alkylthioxanthate) compounds of iron(III) have been previously described and their instability has been noted.[17] The decomposition products were not identified, however. As outlined in the present report, carbon disulfide elimination occurs to form the series of dimeric compounds, $[Fe(SR)(S_2CSR)_2]_2$, the properties of which have been investigated by a variety of physical techniques. A detailed discussion of the crystal structure determination, geometry, and structural evidence for metal–metal bonding in $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ will be taken up separately.[18]

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**Table I.** Analytical and Molecular Weight Data

| Complex | % C |  | % H |  | % S |  | Mol wt[a] |  | Mp,[b] °C |
|---|---|---|---|---|---|---|---|---|---|
|  | Calcd | Found | Calcd | Found | Calcd | Found | Calcd[c] | Found |  |
| $[Fe(S_2CSR)_2(SR)]_2$ |  |  |  |  |  |  |  |  |  |
| R = $C_2H_5$ | 24.6 | 24.4 | 3.86 | 3.62 | 57.3 | 57.0 | 782 | 778 | 140–143 dec |
| R = $n$-$C_3H_7$ | 30.5 | 30.3 | 4.88 | 4.40 | 51.7 | 50.0 | 866 | 865 | 123 dec |
| R = $n$-$C_4H_9$ | 35.4 | 35.3 | 5.72 | 5.81 | 47.2 | 49.5 | 950 | 962 | 112 dec |
| R = $C_6H_5CH_2$ | 47.8 | 47.6 | 3.62 | 3.62 | 39.9 | 39.9 | 1124 | . . .[d] | 148 dec |
| $[Fe(S_2CSC(CH_3)_3)_3]$ | 32.7 | 32.9 | 4.91 | 5.13 | 52.3 | 53.3 | 552 | 553 | 116 |

[a] All determinations were performed in chloroform solutions at ~$10^{-2}$ *M*. [b] Uncorrected. [c] Calculated values are for complex as shown in first column (dimer or monomer). [d] Insufficiently soluble for determination.

## Experimental Section

**General Comments.** All compounds were prepared from the highest purity chemicals available commercially. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Molecular weights were determined at 37° using a Mechrolab vapor pressure osmometer calibrated with benzil. Analytical and molecular weight data are summarized in Table I.

**Sodium Alkylthioxanthate Solutions.** A suspension of white alkyl mercaptide salt was formed by adding an excess of alkanethiol to sodium hydride (2.4 g, 0.1 mol) suspended in 100 ml of THF at 0°. Dropwise addition of 15 ml of carbon disulfide resulted in the formation of yellow solutions of the ligands[17] which were used to prepare the complexes with iron(III).

**Bis(ethylthioxanthato)-$\mu$-bis(ethylthioxanthato)-$\mu'$-bis(ethylthio)-diiron(III), $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$.** The solution of sodium ethylthioxanthate, prepared as described above, was added to 50 ml of an aqueous solution of ferric chloride (4.86 g, 0.03 mol). The mixture was immediately extracted with several portions of ether. Overnight evaporation of the ether solution yielded a crystalline precipitate, which was recrystallized from chloroform-ethanol at 0° as shiny black (red-brown) prisms (yield 5.3 g, 46%).

**Bis(alkylthioxanthato)-$\mu$-bis(alkylthioxanthato)-$\mu'$-bis(alkylthio)-diiron(III), $[Fe(S_2CSR)_2(SR)]_2$ (R = $n$-$C_3H_7$, $n$-$C_4H_9$, $C_6H_5CH_2$).**[19] These complexes were obtained in a manner analogous to that already described for the ethyl compound, except that it was found advantageous to extract the crude products with chloroform, rather than ether. Addition of an excess (50–100% by volume) of methanol resulted, upon standing overnight at 0°, in the formation of shiny black crystalline precipitates. These were recrystallized from carbon disulfide–pentane at 0°. Yields ranged from 40 to 50%.

**Tris($t$-butylthioxanthato)iron(III), $[Fe(S_2CSC_4H_9)_3]$.** The solution of sodium $t$-butylthioxanthate was added to an aqueous solution of ferric chloride (4.86 g, 0.03 mol). Unlike the other alkyl analogs described above, a precipitate formed in a few minutes. Recrystallization at 0° from carbon disulfide–pentane gave black crystals (violet powder) in 43% yield. This complex has been previously prepared and studied by other workers.[17] Although our material melts 18° higher than theirs, it has similar magnetic properties and chemical analysis. The complex was stored at 0° under a nitrogen atmosphere.

**Physical Measurements.** Infrared spectra were obtained with a Perkin-Elmer 621 grating instrument on samples mulled in Nujol in the range 4000–250 cm$^{-1}$; polystyrene was used as the calibrant. Electronic spectra of solutions were recorded on a Cary 14 spectrophotometer at concentrations of $10^{-2}$ to $10^{-5}$ *M* using 1-cm matched quartz cells. Solid-state electronic spectra were taken on a Beckman Model DU spectrophotometer equipped with a reflectance attachment. The highly colored solid samples were diluted with magnesium carbonate. Proton magnetic resonance (pmr) spectra of complexes dissolved in $CS_2$ were recorded on a Varian Associates A-60A or HA-100 spectrometer, both equipped with a variable-temperature probe and spin decoupler. Tetramethylsilane was used as an internal standard. Room-temperature (*ca.* 23°) magnetic susceptibilities of recrystallized, thoroughly dried solids were measured by the Gouy technique, as discussed by Figgis and Lewis.[20] Samples were finely pulverized and packed several times in Gouy tubes calibrated with $Hg[Co(NCS)_4]$. Runs were made at three field strengths and the results averaged to give the final value. The magnetic susceptibility of tris($t$-butylthioxanthato)iron(III) was measured in dichloromethane solution by the method of Evans[21] over the range $210° < T < 293$°K. Dichloromethane was used as the reference solution.[21c]

Conventional voltammetric data were collected with a modified Heath Model EUW-401 polarograph equipped with three-electrode geometry. The experimental procedure was similar to that described by Holm and coworkers.[22,23] Voltammetric measurements were carried out on ~$10^{-3}$ *M* solutions in doubly distilled dichloromethane, with 0.5 *M* tetra-$n$-butylammonium perchlorate as the supporting electrolyte. The working electrode was platinum, rotated synchronously at 600 rpm.[24] The silver–silver iodide reference electrode, contained in a glass tube with an asbestos fiber sealed into one end, was inserted directly into the junction compartment of the cell (Figure 1, ref 22). In order to calibrate and monitor the stability of the system, the successive one-electron oxidations of the $[CrS_6C_6(CN)_6]^{3-}$ and $[NiS_4C_4(CN)_4]^{2-}$ ions[25] were run several times during the course of the studies. Half-wave potentials reported have an estimated precision of ±25 mV.

Triangular wave oscillographic voltammetry[26] was performed on a Chemtrix Model SSP-2 polarograph with a 1.5-mm diameter stationary platinum sphere as the working electrode. Again the three-electrode configuration was used to compensate for the *iR* drop of the cell. Other experimental conditions were similar to those used in the conventional voltammetric studies.

## Results and Discussion

**Preparations.** The synthesis of dimeric complexes of general formula $[Fe(SR)(S_2CSR)_2]_2$ probably occurs according to eq 1, although the tris($n$-alkylthioxanthato)iron(III) complexes were not observed under the experimental conditions employed. Attempts to prepare the previously reported[17] $[Fe(S_2CSC_2H_5)_3]$ compound have thus far been unsuccessful. Molecular weight and analytical data (Table I) together with pmr studies (*vide infra*) of the $n$-alkyl complexes prove them to be diamagnetic dimers of iron, formally in the +3 oxidation state. These compounds may correspond to the diamagnetic materials previously suggested[17] to contain iron(II).

$$2[Fe(S_2CSR)_3] \longrightarrow [Fe(SR)(S_2CSR)_2]_2 + 2CS_2 \qquad (1)$$

$$R = C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9,\ C_6H_5CH_2$$

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(19) The benzyl analog has been reported previously: D. Coucouvanis, Ph.D. Thesis, Case Institute of Technology, 1967.

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(26) Reference 24, p 577 ff.

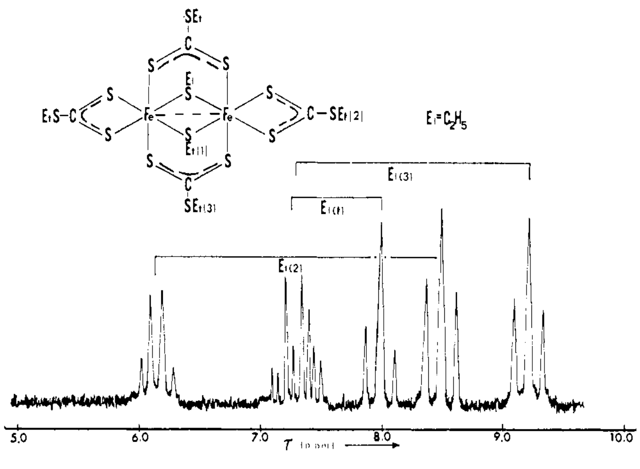
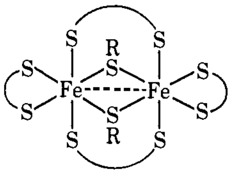


Figure 1. The 100-MHz pmr spectrum of the ethyl dimer in carbon disulfide solution. Brackets identify nonequivalent ethyl groups as determined by spin-decoupling experiments. For discussion of assignment, see text.



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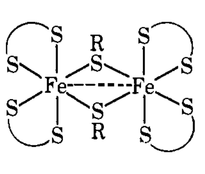

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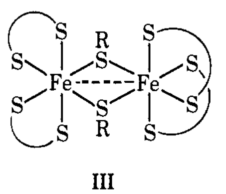
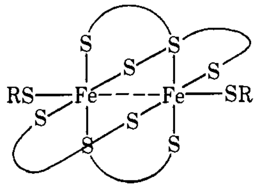


III



IV

For the case where R = $t$-$C_4H_9$, reaction 1 is greatly retarded, and only the known,[17] monomeric tris($t$-butylthioxanthato)iron(III) complex was obtained. Boiling a carbon disulfide solution of this compound failed to promote dimer formation by $CS_2$ elimination, as judged by pmr spectroscopy. Refluxing in toluene led to extensive decomposition and the formation of a brown, insoluble residue. The steric difficulties encountered when two $t$-butyl mercaptide ligands are required to bridge two six-coordinate iron atoms might account for the absence of dimer formation. Aromatic alkylthioxanthate ligands are apparently rather unstable. An attempt to prepare a solution of sodium phenylthioxanthate from thiophenol, sodium hydride, and carbon disulfide failed to produce the desired yellow color of the ligand.

**Molecular Structure and Proton Nmr Studies.** Proton nmr (pmr) spectra of $CS_2$ solutions containing $[Fe(SR)(S_2CSR)_2]_2$, R = $C_2H_5$, $n$-$C_3H_7$, $n$-$C_4H_9$, and $C_6H_5CH_2$, exhibited resonances with line widths and chemical shift values indicative of diamagnetic compounds.[27] A detailed study of the ethyl compound was performed, its pmr spectrum being the least complicated of the group. As shown in Figure 1, the spectrum consists of three equally intense methylene quartets ($J \sim 8$ Hz) centered at $\tau$ 6.25, 7.44, and 7.46 ppm, as well as three methyl triplets ($J \sim 8$ Hz), each $^3/_2$ as intense as the quartets, at $\tau$ 7.95, 8.33, and 9.10 ppm. These results require three chemically distinct ethyl groups of equal concentration. Structures I–IV are in accord with the molecular weight data (Table I), but only I is consistent with the pmr results. Other dimeric structures compatible with the pmr spectrum may be written, but in the absence of supporting evidence, structure I is preferred since it is found to occur in the solid state.[13,18] This structural assignment is also supported by a comparison of reflectance and solution electronic spectra, as will be discussed later.

Attempts to convert structure I into one of its possible isomers by heating resulted in decomposition into black materials, insoluble in $CS_2$. In addition, the possibility of *syn-anti* isomerism,[28a] involving the bridging ethyl mercaptide ligands,[28b] was investigated. In the crystal, $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ is centrosymmetric, with the ethyl groups of the mercaptide ligands *anti* with respect to the plane containing the iron and sulfur atoms.[13,18] In solution, only a single ethyl mercaptide resonance is observed (Figure 1 and following discussion) even at temperatures down to −60°. Three possible interpretations for this behavior are that (1) only one isomer, *syn* or *anti*, exists in solution; (2) both isomers exist but are in rapid equilibrium at temperatures above −60°; (3) both isomers exist in equilibrium but have nearly identical chemical shifts. At present no one of these possibilities can be eliminated.

With the aid of spin-decoupling experiments, the methylene resonance associated with each of the methyl resonances was identified. Irradiation at the center of the $\tau$ 7.95 triplet considerably simplified the $\tau$ 7.45 region, whereas irradiation at $\tau$ 8.33 collapsed the quartet at 6.25 ppm. These results are summarized in Figure 1 and Table II. Table II also includes some chemical shift data for ethyl groups in related molecules.

Table II. Chemical Shift Data for $CH_3CH_2SX$ Groups in $CS_2$ Solutions

| Compound | τ, ppm<br>$CH_2$ quartet | <br>$CH_3$ triplet | $\Delta\tau$,[a] ppm | Group |
|---|---|---|---|---|
| $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ | 6.25 | 8.33 | 2.08 | *b* |
| | 7.44 | 7.95 | 0.51 | *c* |
| | 7.46 | 9.10 | 1.64 | *d* |
| $[Fe(SC_2H_5)(CO)_2(\pi$-$C_5H_5)]$[e] | 8.03 | 8.9 | 0.87 | *c* |
| $[Fe(SC_2H_5)(CO)(\pi$-$C_5H_5)]_2$[e] | 8.39 | 9.28 | 0.89 | *c* |
| $[Fe(S_2CSC_2H_5)(CO)(\pi$-$C_5H_5)]$[f] | 6.85 | 8.63 | 1.78 | *b* |
| $[Ni(S_2CSC_2H_5)_2]$[g] | 6.65 | 8.44 | 1.79 | *b* |

[a] Chemical shift difference between methylene and methyl resonances. [b] Terminal ethyl thioxanthate. [c] Ethyl mercaptide. [d] Bridging ethyl thioxanthate. [e] M. Ahmad, R. Bruce, and G. R. Knox, *J. Organometal. Chem.*, 6, 1 (1966). [f] Reference 4. [g] Reference 15.

Of the three $\Delta\tau$ values (Table II) observed for the ethyl groups in $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$, the smallest probably results from the bridging ethyl mercaptide ligand. Several years ago it was suggested[29] that the

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(27) The molar susceptibility of *solid* $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ was measured to be $\chi_M^{cor} = -70 \times 10^{-6}$ cgs/mol, uncorrected for underlying metal diamagnetism.

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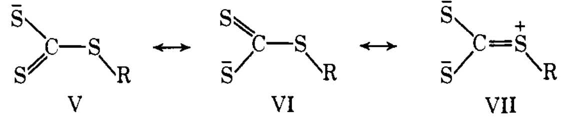
$\Delta\tau$ value of an ethyl group is related to the electron-withdrawal power of its substituent. The $-SCS_2^-$ fragment might be expected to be more electron-withdrawing than $-S^-$, especially since resonance form VII has been shown[18] to contribute significantly to the overall electronic structure of coordinated thioxanthate ligands. Moreover, reference to Table II reveals that the $\Delta\tau$ values for ethyl mercaptide groups are generally smaller than the values for ethylthioxanthate ligands. The resonances at $\tau$ 7.44 and 7.95 ppm have therefore been assigned to the ethyl mercaptide ligands.


V VI VII

The assignment of the two different ethylthioxanthate ligand resonances has also been attempted using similar arguments. Since resonance form VII contributes more to the electronic structure of the terminal thioxanthate ligand than to that of the bridging thioxanthate group,[18] the $\Delta\tau$ value for the former might therefore be expected to be the larger of the two. On this rather tenuous basis, the resonances at $\tau$ 6.25 and 8.33 ppm have been assigned to the terminal ethylthioxanthate group. The chemical shift values of related iron and nickel complexes (Table II) lend some support to this assignment.

A summary of the conclusions of the foregoing analysis of the proton nmr spectrum of $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ appears in Figure 1. Proton nmr spectra obtained for the *n*-propyl and *n*-butyl analogs were qualitatively similar to the ethyl spectrum, but sufficiently complex that no attempt was made to assign the resonances in detail. Chemical shift values are summarized in Table III. The benzyl analog was not very soluble, even in $CS_2$, but its spectrum could be obtained at high spectral amplitudes at 100 MHz. In addition to resonances in the aromatic proton region, lines were observed at $\tau$ values of 5.08, 6.11, 6.22, and 6.38 ppm, some of which showed slight splittings. In view of the limited solubility, the possibility of *syn-anti*[28a] or other types of isomerism was not investigated.

Table III. Chemical Shift Values for $[Fe(SR)(S_2CSR)_2]_2$ Complexes in $CS_2$ Solutions

| R | $\tau$, ppm | | | | | |
|---|---|---|---|---|---|---|
| $C_2H_5$ | 9.10[a] | 8.33[a] | 7.95[a] | 7.46[b] | 7.44[b] | 6.25[b] |
| $n$-$C_3H_7$ | 9.24[c] | | (8.76, 7.98, 7.52)[d] | | | 6.30[a] |
| $n$-$C_4H_9$ | 8.99[c] | | (8.22, 7.45)[d] | | | 6.26[a] |

[a] Triplet. [b] Quartet. [c] Complex multiplet centered approximately at $\tau$ value indicated. [d] Several overlapping resonances with maxima at $\tau$ values indicated.

The complex $[(t\text{-}C_4H_9SCS_2)_3Fe]$ is monomeric (Table I). In both the solid state and solution, at room temperature, the molecule has an observed $\chi_M^{cor}$ of $2530 \times 10^{-6}$ cgs unit/mol, which corresponds to a $\mu_{eff}$ of 2.46 BM. In dichloromethane solution, the variation of $\chi_M^{cor}$, with temperature over the limited range $210° < T < 293°K$, $3610 > \chi_M^{cor} > 2570 \times 10^{-6}$ cgs unit/mol, is in good agreement with temperature-dependent measurements on the solid, previously reported and discussed by Ewald and Sinn.[17] The pmr spectrum of tris(*t*-butylthioxanthato)iron(III) in $CS_2$ solution consists of a fairly broad line ($\Delta\nu_{1/2} = 6$ Hz), as might be expected for a paramagnetic compound, centered at $\tau$ 8.12 ppm. By contrast, the analogous diamagnetic cobalt(III) complex, $[(t\text{-}C_4H_9SCS_2)_3Co]$,[30] exhibits a relatively sharp resonance ($\Delta\nu_{1/2} = 1.5$ Hz) at $\tau$ 8.32 ppm.

**Electronic Structure and Electrochemical Studies.** The observed diamagnetism of the binuclear iron(III) complexes having structure I may be understood in terms of the qualitative molecular orbital arguments introduced before.[13] Complementary analyses using a dipolar coupling model[31] or invoking exchange effects[32] are possible, but are not amenable to quantitative evaluation in this case because the compounds are diamagnetic over the range of their thermal stability. To recapitulate,[13] each iron atom is assigned a set of orbitals for $\sigma$ bonding with the sulfur atoms. The remaining metal d orbitals form a $\sigma(xy)$ MO for Fe–Fe bonding which is populated, a set of four nonbonding or $\pi$-bonding MO's, also populated, and an empty $\sigma^*(xy)$ MO. The fact that all spins are paired implies that the energy gap between the highest occupied orbitals and the $\sigma^*(xy)$ orbital is greater than the pairing energy.

In view of the role of polynuclear, sulfur-coordinated iron complexes in electron-transfer proteins,[33] electrochemical studies of the $[Fe(SR)(S_2CSR)_2]_2$ compounds were performed. The electrochemical behavior of $[Fe(S_2CSR)_3]$, where $R = t\text{-}C_4H_9$, was also observed. The results are presented in Table IV.[34] The iron(III)

Table IV. Electrochemical Data for $[Fe(SR)(S_2CSR)_2]_2$ and $[(t\text{-}C_4H_9SCS_2)_3Fe]$ in Dichloromethane[a]

| Complex | $E_{1/2}$, V[b] | $i_d/C$, $\mu A/mM$[c] | Type[d] | $n$(apparent)[e] |
|---|---|---|---|---|
| $[(C_2H_5SCS_2)_2(C_2H_5S)Fe]_2$ | −0.65 | 173 | red(i) | 2 |
| | +0.76 | 78 | ox(i) | 1 |
| $[(n\text{-}C_3H_7SCS_2)_2(n\text{-}C_3H_7S)Fe]_2$ | −0.64 | 153 | red(i) | 2 |
| | +0.79 | 77 | ox(i) | 1 |
| $[(n\text{-}C_4H_9SCS_2)_2(n\text{-}C_4H_9S)Fe]_2$ | −0.71 | 163 | red(i) | 2 |
| | +0.70 | 88 | ox(i) | 1 |
| $[(t\text{-}C_4H_9SCS_2)_3Fe]$ | −0.36 | 80 | red(r) | 1 |
| | +0.73 | 74 | ox(r) | 1 |
| $[NiS_4C_4(CN)_4]^{2-}$[f] | +0.35 | 80 | ox(r) | 1 |
| | +1.35 | 76 | ox(r) | 1 |
| $[CrS_6C_6(CN)_6]^{3-}$[g] | +0.03 | 85 | ox(r) | 1 |
| | +0.69 | 87 | ox(r) | 1 |

[a] Using 0.5 $M$ $[(n\text{-}C_4H_9)_4N](ClO_4)$ as supporting electrolyte and a rotating platinum working electrode. [b] *Vs.* Ag|AgI reference electrode. [c] Concentration calculated on the basis of formulas given in the first column. [d] red = reduction, ox = oxidation, i = irreversible as judged by cyclic voltammetry (Figure 2), r = reversible. [e] Apparent number of electrons involved in electrode process, estimated by comparing current densities (third column) with the values obtained on our apparatus for the one-electron oxidations of known compounds (compare last two entries in table). [f] Data are for $(-2 \rightarrow -1)$ and $(-1 \rightarrow 0)$ oxidation.[9] [g] Data are for the $(-3 \rightarrow -2)$ and $(-2 \rightarrow -1)$ oxidations.[9]

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**Table V.** Electronic Spectral Bands of Iron(III) Thioxanthate Complexes[a]

| Compound | State[b] | Absorption maxima, $cm^{-1} \times 10^{-3}$ Band 1 | Band 2 | Band 3 | Band 4 | Band 5 |
|---|---|---|---|---|---|---|
| $[Fe(SR)(S_2CSR)_2]_2$ | | | | | | |
| R = $C_2H_5$ | Solution | 8.66 (1.73) | 12.70 (1.90) | 19.95 (3.85) | 24.90 (4.20) | 32.10 (5.0) |
| | Solid | *c* | *c* | 20.0 | 25.0 | 32.3 |
| R = *n*-$C_3H_7$ | Solution | 8.73 (1.69) | 12.80 (1.91) | 19.80 (3.78) | 24.60 (4.20) | 31.80 (4.95) |
| | Solid | *c* | *c* | 19.8 | 24.50 | 32.3 |
| R = *n*-$C_4H_9$ | Solution | 8.70 (1.71) | 12.82 (1.93) | 19.95 (3.82) | 24.70 (4.23) | 31.40 (4.97) |
| | Solid | *c* | *c* | 19.7 | 24.39 | 32.25 |
| R = $C_6H_5CH_2$ | Solution | 8.65 (1.70) | 12.75 (1.92) | 19.65 (3.83) | 24.20 (4.28) | 32.40 (5.22) |
| | Solid | *c* | *c* | 19.8 | 25.0 | 32.3 |
| $[Fe(S_2CSR)_3]$ | | | | | | |
| R = *t*-$C_4H_9$ | Solution | *d* | *d* | 18.60 (3.72) | ~25.0 (sh)[e] | 31.20 (4.66) |
| | Solid | *c* | *c* | 18.8 | 25.0 | 32.5 |

[a] Numbers in parentheses are molar extinction coefficients (log $\epsilon_{max}$). [b] Solution spectra in $CHCl_3$, solids by reflectance spectroscopy. [c] Low-intensity bands were difficult to discern in the solids. [d] Possible absorptions obscured by intense ($\epsilon \sim 100$) tail of higher energy band (see Figure 3). [e] Band appeared as a shoulder on the side of a more intense transition.

dimers exhibit a two-electron reduction wave and a one-electron oxidation wave, both irreversible (Figure 2) at scan rates of 1 V/sec. One possible explanation for the irreversibility of the two-electron reduction process is that the $\sigma^*(xy)$ orbital becomes populated in a rapid electron-transfer step, following which a slow molecular rearrangement (*e.g.*, I → II) occurs. This suggestion is supported by the fact that the analogous cobalt(III) complexes, $[Co(SR)(S_2CSR)_2]_2$, are known[30] to have structures in solution different from I. Alternatively, the addition of two electrons to the dimer might result in irreversible cleavage to monomeric iron(II) compounds, as was postulated[23] for the irreversible two-electron reduction of $[FeS_4C_4(CN)_4]_2^{2-}$. Discussion of the irreversibility of the one-electron oxidation will be taken up later.[30]

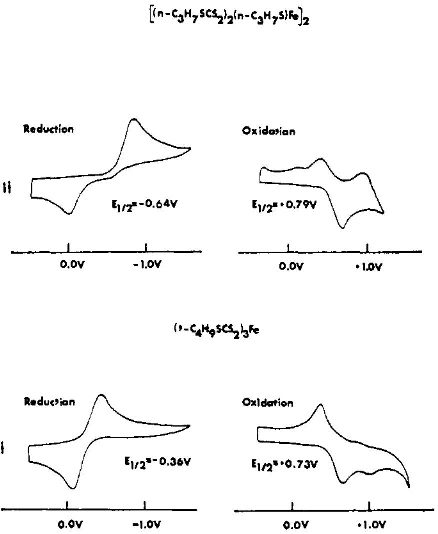

Figure 2. Representative cyclic voltammograms of iron(III) thioxanthate complexes: $10^{-3}$ *M* in dichloromethane solution, 1 V/sec scan rate.

The monomeric *t*-butyl complex exhibits reversible redox behavior (Figure 2);[26] plots of (scan speed)$^{1/2}$ against peak current gave straight lines passing through the origin.[36] The products, presumed to be $[Fe(S_2CSR)_3]^-$ and $[Fe(S_2CSR)_3]^+$, have not yet been isolated. Although the electrochemical activity of 1,1-dithio complexes[14] has not been nearly so well investigated as that of related 1,2-dithio complexes,[9] the present observation of reversible oxidation–reduction waves for tris(*t*-butylthioxanthato)iron(III) offers some indication that, at least in certain cases, 1,1-dithio compounds can also partake in facile electron-transfer reactions.

**Electronic and Infrared Spectral Studies.** Summarized in Table V are the electronic spectral bands of the various complexes, from which certain general conclu-

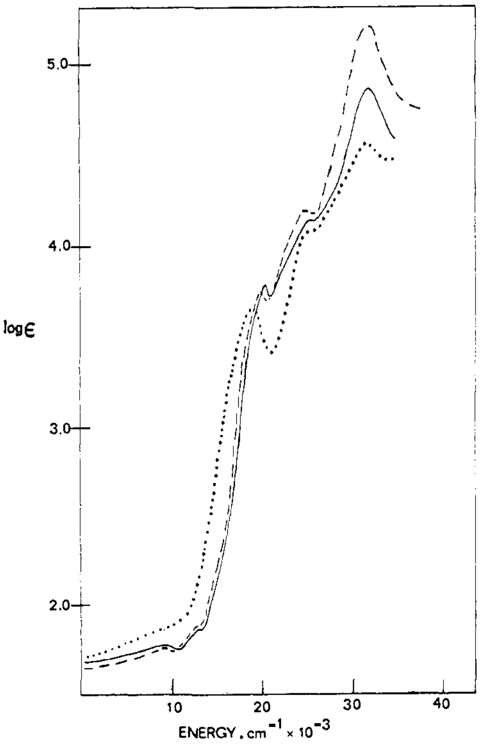

Figure 3. Uv-visible spectra of $[(C_2H_5SCS_2)_2(C_2H_5S)Fe]_2$ (———), $[(C_6H_5CH_2SCS_2)_2(C_6H_5CH_2S)Fe]_2$ (- - - -), and $[(t-C_4H_9SCS_2)_3Fe]$ (. . . .) in chloroform solutions.

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[34] The half-wave potentials in Table IV for the ethyl dimer are considered to be more reliable than the preliminary values reported previously.[35]

[35] D. Coucouvanis, S. J. Lippard, B. G. Segal, and J. A. Zubieta, *Proc. Int. Conf. Coord. Chem., 12th, Sydney, 1969*, 190 (1969).

[36] R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

sions may be drawn. From the close agreement between the solution and diffuse reflectance spectra for each compound, it appears that no gross structural change occurs when the compounds dissolve. Moreover, there are significant qualitative differences between the spectra of the dimers and that of the monomer (Figure 3), particularly in bands 1-3 (Table V). This information is useful in characterizing the benzyl complex as a sulfur-bridged iron(III) *dimer* in solution, the benzyl compound being insufficiently soluble (Table I) for a molecular weight determination. Also, the similarity in the electronic spectra of the dimeric complexes, together with the qualitative similarities in their pmr spectra (with the possible exception of the benzyl analog) (Table III), suggests that the compounds are structurally identical. Since the ethyl dimer is known to have structure I in the crystalline state,[13] it seems likely from the foregoing discussion that all the dimers have this structure, both in the solid and in solution.

Recent reviews[14,37] of the spectra and electronic structure of complexes with sulfur-containing ligands reveal that little work has been done on thioxanthate compounds, although xanthates have been more extensively investigated. From their intensity and the fact that they are common to both monomeric and dimeric iron(III) complexes, bands 3, 4, and 5 (Table V) appear to be either change-transfer or ligand internal transition absorptions. In $[(C_2H_5SCS_2)_3Fe]$, a low-energy band at 8800 $cm^{-1}$ was observed and assigned to the $^2T_2$-$^4T_1$ transition.[17] No such band could be discerned in the spectrum of the *t*-butyl analog, dissolved in chloroform, despite extensive efforts (changing slit program or cell path length) to identify one. The shift of band 3 to lower energies in the monomer compared to the dimer increased the intensity of its tail in the region of band 1 (Figure 3), which may account for the difficulty in seeing the weak $^2T_2$-$^4T_1$ transition. Using carbon disulfide as a solvent, a broad absorption centered at 8200 $cm^{-1}$ ($\epsilon \sim 5$) was observed for $[(t\text{-}C_4H_9SCS_2)_3Fe]$. An X-ray structural investigation of this complex would be of interest.

**Table VI.** Summary of Selected Infrared Spectral Frequencies for Iron(III) Thioxanthate Complexes[a,b]

| Complex | Frequency, $cm^{-1}$ | | | | |
|---|---|---|---|---|---|
| $[Fe(SR)(S_2CSR)_2]_2$ | | | | | |
| R = $C_2H_5$ | 1054[c] | 999 | 981 (s) | 949 (s) | 875 (s)[d] |
| R = $n$-$C_3H_7$ | 1080 | 1011[d] | 979 (s) | 955 (s) | 880 (s)[c] |
| R = $n$-$C_4H_9$ | 1095 | 1019 | 982 (s) | 955 (s) | 887 (s) |
| R = $C_6H_5CH_2$ | 1058 | 1019 | 984 (s)[c] | 965 (s) | 874 (s) |
| $[Fe(S_2CSC(CH_3)_3)_3]$ | 1060 (sh) | 1021 | 977 (s) | 921 (s) | |

[a] Samples mulled in Nujol. [b] Absorptions are of medium intensity unless otherwise indicated (s = strong, sh = shoulder). [c] Low-energy shoulder observed on band. [d] High-energy shoulder on band.

A compilation of the more prominent infrared spectral absorption bands between 800 and 1100 $cm^{-1}$ is presented in Table VI. Unfortunately, these absorptions provide little information about the relative contributions of resonance forms V-VII to the electronic structure of coordinated thioxanthate ligands, in contrast to similar data for xanthate and dithiocarbamate complexes.[14,38] A recent analysis[39] of the vibrational spectra of metal xanthate complexes identifies bands $\sim$1115 and 1025 $cm^{-1}$ with $\nu$ ($C\overset{\cdots}{-}S$), and $\sim$474 $cm^{-1}$ with $\nu$ (M—S), where M is Ni, Co, or Cr. The band of medium intensity occurring between 999 and 1021 $cm^{-1}$ in all the iron complexes (Table VI) probably has considerable $C\overset{\cdots}{-}S$ character. The two strong absorptions between 920 and 985 $cm^{-1}$ appear to be characteristic of the $SCS_2$ fragment, since they do not appear in the spectra of related xanthate complexes.[39] A scan of the low-energy infrared region revealed two sharp bands of medium intensity at 474 and 482 $cm^{-1}$ for $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$, which are tentatively assigned as Fe–S stretching frequencies.

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