

EPR spectra were recorded on a Varian V-4510 or a Bruker B-ER420 instrument, and EPR parameters were evaluated as described.<sup>21</sup> The complexes were determined to be  $90 \pm 10\%$  EPR active by comparison of their EPR signals with the EPR signals from  $\text{MoOCl}(\text{ox})_2$ , which had been calibrated by double integration against the EPR signal from  $\text{K}_3\text{Mo}(\text{CN})_6$ . Samples were prepared under prepurified  $\text{N}_2$  (99.997%), transferred to 3.0-mm i.d. tubes with the use of gas-tight syringes, and frozen immediately in liquid nitrogen for low-temperature spectra. For room-temperature spectra, samples were transferred to a flat cell that had been evacuated and flushed with  $\text{N}_2$  and kept under argon until spectra were recorded. Generally,

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$0.1 \text{ M } (\text{C}_2\text{H}_5)_4\text{NCl}$  was added to the solutions of the W(V) complexes, approximately  $5.00 \times 10^{-4} \text{ M}$  in DMF, for stabilization.

Infrared spectra were recorded on a Beckman IR 20 instrument with the use of Nujol mulls.

**Acknowledgment.** This work was supported by Grant No. GM-08347 from the National Institutes of Health.

**Registry No.** *cis*- $\text{WOC}l_3(\text{bpy})$ , 77340-55-7; *trans*- $\text{WOC}l_3(\text{bpy})$ , 77285-89-3; *trans*- $\text{WOC}l_3(\text{phen})$ , 77224-45-4; *cis*- $\text{WOC}l(\text{ox})_2$ , 77224-46-5; *cis*- $\text{WOC}l(\text{tox})_2$ , 77224-47-6;  $\text{WO}_2\text{Cl}_2(\text{bpy})$ , 18252-71-6;  $\text{WO}_2\text{Cl}_2(\text{phen})$ , 18252-72-7;  $\text{WO}_2(\text{ox})_2$ , 21289-71-4;  $\text{WO}_2(\text{tox})_2$ , 55835-57-9;  $\text{WO}_2\text{Br}_2(\text{bpy})$ , 12116-32-4;  $\text{WO}_2(\text{acac})_2$ , 21292-49-9;  $\text{WOC}l_3(\text{THF})_2$ , 18131-65-2;  $[(\text{CH}_3)_4\text{N}]_2[\text{WOC}l_5]$ , 77224-48-7;  $\text{WO}_2\text{Cl}_2(\text{OP}(\text{C}_6\text{H}_5)_3)_2$ , 18252-68-1.

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## Iron-Sulfur Stretching Band Assignments in High-, Low-, and Mixed-Spin Iron(III) Dialkyldithiocarbamates

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Received October 6, 1980

The far-infrared spectra of several iron(III) dialkyldithiocarbamates having room-temperature magnetic moments in the high-, low- and intermediate-spin range have been reinvestigated. Iron-sulfur stretching vibrations have been assigned with the use of  $^{54}\text{Fe}$  and  $^{56}\text{Fe}$  isotopes. The high-spin Fe-S stretching vibrations appear at  $205\text{--}250 \text{ cm}^{-1}$  and the low spin at  $305\text{--}350 \text{ cm}^{-1}$ , and the intermediate spin show Fe-S stretching bands in both regions. Results of spectral measurements above and below room temperature are explained on the basis of these assignments.

### Introduction

The ability of dialkyldithiocarbamate ( $\text{R}_2\text{dtc}$ ) ligands to stabilize iron(III) in high-spin, low-spin, and "intermediate"-spin magnetic moment arrangements has been recognized and investigated with the use of a variety of methods.<sup>2-14</sup> In the far-infrared spectral region, vibrational spectroscopy has been employed because metal-ligand stretching bands which appear in this region may provide information about the strength of the metal-ligand bonds and the symmetry of the molecule. Such data are also used in calculating the value of the partition function,<sup>7</sup> estimating a value for the entropy of the systems,<sup>15</sup> and distinguishing between models of the "intermediate" spin systems.<sup>8</sup> For this information to be useful, the metal-ligand stretching bands should be correctly assigned. Although some progress has been realized in the assignment of the Fe-S stretching bands for

Table I. Previous  $\nu(\text{Fe-S})$  Assignments in  $\text{Fe}(\text{R}_2\text{dtc})_3$

compd	high-spin	low-spin	ref
$\text{Fe}[(\text{pyr})\text{dtc}]_3$	328		8
$\text{Fe}[(\text{pyr})\text{dtc}]_3$	320		5
$\text{Fe}[(\text{pyr})\text{dtc}]_3$	334, 324 <sup>a</sup>		7
$\text{Fe}(i\text{-Pr}_2\text{dtc})_3$		365, 320	5
$\text{Fe}(N,N\text{-c-Hx}_2\text{dtc})_3$		346	8
$\text{Fe}(\text{Me}_2\text{dtc})_3$	360	334, 305	7
$\text{Fe}(N\text{-Et-N-Phdtc})_3$	304 <sup>b</sup>	341 <sup>b</sup>	8
$\text{Fe}(\text{Et}_2\text{dtc})_3$	355	552	14
$\text{Fe}(\text{Pr}_2\text{dtc})_3$	307	367	7

<sup>a</sup> Measured at 30 K. <sup>b</sup> Assigned on the basis of  $^{54}\text{Fe}/^{56}\text{Fe}$ .

these iron(III) complexes, conflicting assignments remain unresolved in several instances. The appearance of ligand absorptions in the same region as the Fe-S stretching bands have made assignments more difficult.

Presently there are four principal investigations in the literature which discuss the Fe-S stretching band assignments in these complexes. These assignments are summarized in Table I. Ewald et al. proposed the  $300\text{--}400\text{-cm}^{-1}$  region for both high- and low-spin Fe-S stretching bands from their study of five  $\text{Fe}(\text{R}_2\text{dtc})_3$  complexes at room and liquid air temperatures.<sup>5</sup> Hall and Hendrickson extended the previous study by investigating a larger number of  $\text{Fe}(\text{R}_2\text{dtc})_3$  complexes plus related compounds and improving the resolution at lower temperatures.<sup>7</sup> They also assigned all Fe-S stretching bands in the  $300\text{--}400\text{-cm}^{-1}$  region, placing the high-spin Fe-S stretching modes at higher energy than the low-spin Fe-S stretching modes. Butcher, Ferraro, and Sinn examined the far-infrared spectra of four  $\text{Fe}(\text{R}_2\text{dtc})_3$  complexes using variable pressures and employing  $^{54}\text{Fe}\text{--}^{56}\text{Fe}$  isotopic substitution for one,  $\text{Fe}(N\text{-Et-N-Phdtc})_3$ .<sup>8</sup> These authors assigned the high-spin Fe-S stretch at lower energy than the low-spin Fe-S stretching modes but kept both in the  $300\text{--}400\text{-cm}^{-1}$  region. More recently, Sorai studied the variable-temperature far-infrared spectra of  $\text{Fe}(\text{Et}_2\text{dtc})_3$  and assigned the low-spin Fe-S

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- (14) M. Sorai, *J. Inorg. Nucl. Chem.*, **40**, 1031 (1978).
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stretching mode at 552 cm<sup>-1</sup> while placing the high-spin Fe-S stretching mode at 355 cm<sup>-1</sup>.<sup>14</sup>

In this work we have reinvestigated the Fe-S stretching band region in a series of Fe(R<sub>2</sub>dtc)<sub>3</sub> complexes representing high-spin, low-spin, and "intermediate" temperature-dependent magnetic moment compounds using <sup>54</sup>Fe and <sup>57</sup>Fe substitution with variable temperature to aid in the spectral interpretation. The information obtained from this investigation should clarify several questions which remain in the present literature assignments and provide data for comparison with other crossover systems.

### Experimental Section

**Preparations.** All chemicals were of the highest grade commercially available. The natural abundance compounds were synthesized by the general methods described in the literature.<sup>13</sup> Isotopic Fe<sub>2</sub>O<sub>3</sub> (90% enriched <sup>54</sup>Fe and <sup>57</sup>Fe purchased from Oak Ridge National Laboratory) was reduced to metallic <sup>54</sup>Fe and <sup>57</sup>Fe by passing hydrogen gas over the oxide at 400 °C. Tris(pyrrolidinedithioato)iron(III) was prepared in the following manner. To 3.0 mg of isotopic iron (<sup>54</sup>Fe) in a 10-mL beaker was added 1 drop of 70% perchloric acid and 5 mL of ethanol. When the iron was totally dissolved, 2 drops of hydrogen peroxide were added and the solution was then heated almost to dryness. The residual liquid was removed through evaporation, and to the resulting solid ferric perchlorate were added dropwise with constant stirring 28.0 mg (slight excess) of freshly prepared sodium pyrrolidinedithioate and 5 mL of ethanol. The resulting black precipitate was stirred for 1 h, filtered, extracted with chloroform, and reprecipitated from ethanol. The sodium pyrrolidinedithioate was prepared as stated in the literature.<sup>26</sup> Other isotopic complexes were prepared following the general described above.

**Spectra.** Most spectra were recorded on the Beckman IR-12 (4000–400 cm<sup>-1</sup>) and the Hitachi Perkin-Elmer FIS-3 (400–100 cm<sup>-1</sup>) spectrophotometers as Nujol mulls on CsI (4000–300 cm<sup>-1</sup>) and/or polyethylene (400–100 cm<sup>-1</sup>) plates. The spectra were recorded at scanning speeds of 1–4 cm<sup>-1</sup>/min. Reproducibility was checked by multiple scans over the desired frequency range; the average error in frequency was ±0.5 cm<sup>-1</sup>. The low-temperature spectra in the 600–400-cm<sup>-1</sup> region were recorded with a specially built cold cell with liquid nitrogen as the coolant. The low-temperature spectra in the 400–100-cm<sup>-1</sup> region were recorded with the use of a slightly modified cold cell which fitted the evacuated sample chamber of the FIS-3, with liquid nitrogen used as the coolant. Calibration of the frequency readings was made with polystyrene for the IR-12 while the FIS-3 was calibrated in single beam mode against the spectra of water vapor.

The infrared spectra of natural abundance and <sup>54</sup>Fe(Et<sub>2</sub>dtc)<sub>3</sub> were obtained with the use of a Digilab FTS-20C vacuum Fourier transform infrared spectrometer using a 6.25-micron mylar beam splitter. A triangular apodization function was used to eliminate spectral feet, and 500 scans were averaged for each spectrum. These spectra were obtained from Nujol mulls between polyethylene plates. The room-temperature spectra were obtained with use of the evacuated bench to eliminate water vapor. The high- and low-temperature spectra were obtained with use of a N<sub>2</sub> purge system. The low-temperature spectra were obtained with use of a liquid-nitrogen cooled sample holder inside an evacuable cell with polyethylene windows. The high-temperature spectra were obtained with use of resistively heated metal sample holder and polyethylene plates.

**Analyses.** Calculated for tris(*N,N*-dimethyldithiocarbamato)iron(III): C, 23.2; H, 4.3; N, 10.1. Found: C, 23.4; H, 4.3; N, 10.0. Calculated for tris(*N,N*-diisopropyldithiocarbamato)iron(III): C, 43.1; H, 7.2; N, 7.2. Found: C, 43.2; H, 7.2; N, 7.0. Calculated for tris(pyrrolidinedithioato)iron(III): C, 36.4; H, 3.9; N, 8.5. Found: C, 36.7; H, 4.8; N, 8.4. Calculated for tris(*O,O'*-diethyl dithiophosphato)iron(III): C, 23.6; H, 4.9. Found: C, 23.8; H, 5.0. Calculated for tris(diethyldithiocarbamato)iron(III): C, 35.98; H, 6.05; N, 8.39. Found: C, 35.80; H, 5.95; N, 8.43.

### Results and Discussion

The general approach followed in applying the results from metal-isotopic measurements to the interpretation of this spectral region have been discussed elsewhere.<sup>16</sup> When the

**Table II.** Low-Frequency Infrared Spectra (500–100 cm<sup>-1</sup>) of Tris(*O,O'*-diethyl dithiophosphato)iron(III) and Tris(pyrrolidinedithioato)iron(III) at 298 K

<sup>54</sup> Fe(Et <sub>2</sub> dtc) <sub>3</sub> IR, cm <sup>-1</sup>	Δν <sup>a</sup>
452.1 w	0.2
397.0 m	0.3
359.1 m	0.2
329.0 sh	<i>c</i>
277.0 s	0.1
208.5 s	3.2
<sup>54</sup> Fe[(pyr)dtc] <sub>3</sub> IR, cm <sup>-1</sup>	Δν <sup>a</sup>
451.8 vw	0.4
419.9 m	0.0
322.8 s	0.5
262.1 m	1.3
238.0 m	2.2
213.2 s	2.2
161.3	0.4

<sup>a</sup> Δν = ν(<sup>54</sup>Fe) – ν(<sup>57</sup>Fe). <sup>b</sup> Italic bands are ν(Fe-S) bands.  
<sup>c</sup> Too weak to determine accurate isotopic shifts.

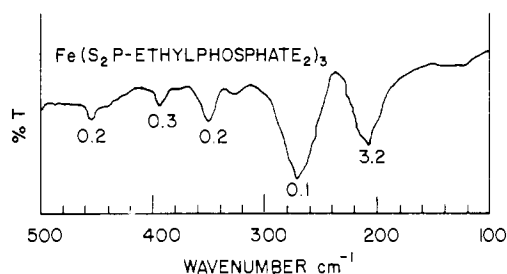
simple harmonic oscillator approximation is applied to an Fe-S stretching band it yields an isotopic frequency ratio, ν<sub>54</sub>/ν<sub>57</sub> = 1.01, where ν is the stretching frequency.<sup>17</sup> The largest possible value for this ratio is 1.027 when only the iron masses are considered. Consequently, isotopic shifts in the range of 2.0–9.6 cm<sup>-1</sup> are expected for Fe-S stretching bands appearing in the 200–350-cm<sup>-1</sup> region. If coupling or overlap of the Fe-S stretching bands with ligand modes occurs, the isotopic shift may be less than that predicted for the pure Fe-S stretch. Bands due solely to the motion of the ligand will not be affected by substitution of the metal. Metal-ligand bending modes normally show much smaller isotopic shifts and appear at lower energy than metal-ligand stretching bands.

The compounds investigated are all pseudooctahedral and have three infrared active Fe-S stretching bands, A<sub>2</sub> and 2E. In most cases we were not able to identify all three because of low intensity, degeneracy, and/or ligand band overlap.

**High-Spin Complexes.** The pyrrolidinedithioato ligand stabilizes iron(III) in the high-spin form.<sup>5</sup> The far-infrared spectrum of this complex is available in ref 5 and 7, while the <sup>54</sup>Fe/<sup>57</sup>Fe isotopic shifts for the bands in the 150–500-cm<sup>-1</sup> region at room temperature measured in this work are listed in Table II. Two bands at 238 and 213 cm<sup>-1</sup> which show isotopic shifts of 2.2 cm<sup>-1</sup> are assigned as Fe-S stretching modes. Four other bands were observed to have shifts of 0.5 cm<sup>-1</sup> or less; these are absorptions due to primarily ligand motions. A broad band at 262.1 cm<sup>-1</sup> shifts 1.3 cm<sup>-1</sup>, less than one-half the expected amount for an Fe-S stretching band. We suggest that this band may be a ligand band partially coupled to a metal-dependent motion. Little change in the position of the bands or the size of their isotopic shift occurs upon cooling, although at ~100 K the 238.0-cm<sup>-1</sup> band is split into two bands, and Hall reports that the 322.8-cm<sup>-1</sup> band also shows two minima at 30 K.<sup>18</sup>

The above assignment of the high-spin Fe-S stretching bands is 80–100 cm<sup>-1</sup> lower than the previous assignments. To confirm our assignment we used the *O,O'*-diethyl dithiophosphate (Et<sub>2</sub>dtc) ligand to form a six-coordinate complex with iron(III) in the high-spin arrangement.<sup>5</sup> In this ligand the C-N bond of the dtc ligand is replaced by a P-O bond, but sulfur remains the coordinating ligand; consequently the Fe-S stretching bands of Fe(Et<sub>2</sub>dtc)<sub>3</sub> and Fe[(pyr)dtc]<sub>3</sub> (pyr

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(17) Substituting the appropriate mass values into the equation for Fe-S ν<sub>54</sub>/ν<sub>57</sub> = hc(k<sub>54</sub>/μ<sub>54</sub>)<sup>1/2</sup>/hc(k<sub>57</sub>/μ<sub>57</sub>)<sup>1/2</sup> yields ν<sub>54</sub>/ν<sub>57</sub> = 1.01, assuming that *k*, the force constant, is unchanged by isotopic substitution.  
(18) G. R. Hall, Dissertation, University of Illinois, 1975.



**Figure 1.** Infrared spectra of iron tris(diethyl dithiophosphate), showing the  $\nu(^{54}\text{Fe})-\nu(^{57}\text{Fe})$  band shifts.

**Table III.** Low-Frequency Infrared Spectra (500–100  $\text{cm}^{-1}$ ) of  $\text{Fe}(i\text{-Pr}_2\text{dtc})_3$  at 298 K: A Low-Spin Complex

$^{54}\text{Fe}(i\text{-Pr}_2\text{dtc})_3$ IR, $\text{cm}^{-1}$	$\Delta\nu^a$
475.4 m	0.3
408.5 m	0.2
365.7 s	2.0
320.9 s	1.2
291.3 w	0.3
264 w	<i>c</i>

<sup>a</sup>  $\Delta\nu = \nu(^{54}\text{Fe}) - \nu(^{57}\text{Fe})$ . <sup>b</sup> Italic bands are  $\nu(\text{Fe-S})$  bands.  
<sup>c</sup> Too weak to determine accurate isotopic shifts.

= pyrrolidyl) should appear in a similar spectral region. The far-infrared spectrum is reported in Figure 1 and Table II with the  $^{54}\text{Fe}/^{57}\text{Fe}$  isotopic shifts. An Fe-S stretching band appears at 208.5  $\text{cm}^{-1}$  which shifts 3.2  $\text{cm}^{-1}$ , substantiating this as the high-spin Fe-S stretching region. This is also the region high-spin Fe<sup>II</sup>-N stretching bands have been found.<sup>15,19,20</sup>

**Low-Spin Complexes.** The far-infrared spectrum of the room-temperature low-spin  $\text{Fe}(i\text{-Pr}_2\text{dtc})_3$  is in ref 5 and 7 and the effect of metal-isotope substitution is given in Table III. The result of the  $^{54}\text{Fe}/^{57}\text{Fe}$  study supports the previous assignment of the 365.1- $\text{cm}^{-1}$  band as an Fe-S stretching band. Below 300  $\text{cm}^{-1}$  only weak bands appear which do not shift significantly in this room-temperature spectrum. This is consistent with the absence of high-spin Fe-S stretching bands. The 320.1- $\text{cm}^{-1}$  band shifts only 1.2  $\text{cm}^{-1}$ , indicating a ligand band coupled with metal motion.

Butcher et al. reported the  $\text{Fe}[(\text{c-Hx})_2\text{dtc}]_3$  spectrum at room temperature shows a band at 346  $\text{cm}^{-1}$  which they assigned to an Fe-S stretching mode based on pressure broadening studies.<sup>8</sup> These low-spin Fe(III)-S stretching bands appear somewhat lower in energy than some low-spin Fe(II)-N containing compounds<sup>19,20</sup> but are similar in position to those of  $\text{Fe}(2\text{-OMePhen})_3$ .<sup>15</sup>

**Mixed-Spin Complexes.** The far-infrared spectra of  $\text{Fe}(\text{Me}_2\text{dtc})_3$  and  $\text{Fe}(\text{Et}_2\text{dtc})_3$  which show "intermediate" temperature-dependent magnetic moments have been reported in several previous studies.<sup>5,7,8,14</sup> These studies (see Table I) have placed both high- and low-spin Fe-S in the 300–400- $\text{cm}^{-1}$  region with the exception of Sorai,<sup>14</sup> who assigned a low-spin Fe-S stretch at 552  $\text{cm}^{-1}$ . An isotopic substitution investigation of another mixed-spin complex did not present results in the 200–300- $\text{cm}^{-1}$  region, and some question exists concerning the size of one of the isotopic shifts.<sup>8,21</sup> The results of our metal-isotopic substitution study on these spectra are given in Table IV.

The room-temperature  $\text{Fe}(\text{Me}_2\text{dtc})_3$  spectrum has bands with the largest  $^{54}\text{Fe}/^{57}\text{Fe}$  isotopic shifts at 338.0 and 235.0

**Table IV.** Low-Frequency Infrared Spectra (500–100  $\text{cm}^{-1}$ ) of  $\text{Fe}(\text{Me}_2\text{dtc})_3$  and  $\text{Fe}(\text{Et}_2\text{dtc})_3$ : Mixed-Spin Complexes

$\text{Fe}(\text{Et}_2\text{dtc})_3$			
298 K		~150 K	
IR, $\text{cm}^{-1}$ <sup>c</sup>	$\Delta\nu^a$	IR, $\text{cm}^{-1}$ <sup>c</sup>	$\Delta\nu^a$
433.2 m	0.0	433.2	0.0
394.6 m	0.0	392.7	0.0
357.0 s	1.0	346.4	1.0
336.7 m	2.9	333.8	1.9
236.4 m	3.9	320.3	0.0
180 w	<i>d</i>	304.9	1.9
		255.7	1.9
$\text{Fe}(\text{Me}_2\text{dtc})_3$			
298 K		100 K	
IR, $\text{cm}^{-1}$ <sup>c</sup>	$\Delta\nu^b$	IR, $\text{cm}^{-1}$ <sup>c</sup>	$\Delta\nu^b$
445.2 s	0.2	446.2 sh	<i>a</i>
		442.0 s	0.2
		408.3 w	0.3
362.2 s	1.4		
338.0 m	2.5	342.2 s	1.3
305 w	<i>d</i>	304.9 m	1.8
275 w	<i>d</i>	254 m	1.5
235.0 s	2.0		
195 w	<i>d</i>	178.0 w	<i>d</i>

<sup>a</sup>  $\Delta\nu = \nu(^{54}\text{Fe}) - \nu(^{55,85}\text{Fe})$ . <sup>b</sup>  $\Delta\nu = \nu(^{54}\text{Fe}) - \nu(^{57}\text{Fe})$ . <sup>c</sup> Italic bands are  $\nu(\text{Fe-S})$  bands. <sup>d</sup> Too weak to obtain accurate isotopic shifts measurements.

$\text{cm}^{-1}$ . In the  $\text{Fe}(\text{Et}_2\text{dtc})_3$  spectrum analogous bands appear at 336.7 and 236.4  $\text{cm}^{-1}$ . These are assigned as Fe-S stretching bands. The appearance of the higher energy Fe-S stretching bands near the position of the Fe-S stretching bands in low-spin complexes and the lower energy Fe-S stretching bands near Fe-S absorptions in  $\text{Fe}[(\text{pyr})\text{dtc}]_3$  is evidence of both high- and low-spin forms being present in  $\text{Fe}(\text{Me}_2\text{dtc})_3$  and  $\text{Fe}(\text{Et}_2\text{dtc})_3$  at room temperature. This conclusion has been previously suggested but was based on different assignments.<sup>7</sup> In the spectra of both these compounds, bands near 360  $\text{cm}^{-1}$  have only a small isotopic shift and are assigned as predominantly ligand modes coupled with a metal-dependent mode or ligand modes which obtain their shift from the nearby metal-ligand stretching modes. Very weak bands at 305 and 275  $\text{cm}^{-1}$  appear in the  $\text{Fe}(\text{Me}_2\text{dtc})_3$  spectrum but are not present in the  $\text{Fe}(\text{Et}_2\text{dtc})_3$  room-temperature spectrum. Accurate isotopic shift data were not obtained on these bands because of their low intensity. This was also the case for a weak band below 200  $\text{cm}^{-1}$  in both  $\text{Fe}(\text{Me}_2\text{dtc})_3$  and  $\text{Fe}(\text{Et}_2\text{dtc})_3$  spectra.

The effect of temperature variation on the far-infrared spectra of mixed-spin complexes has been examined previously from 30–300 K.<sup>5,7,8,14</sup> In this work we have extended the temperature range to 373 K.

Both  $\text{Fe}(\text{Me}_2\text{dtc})_3$  and  $\text{Fe}(\text{Et}_2\text{dtc})_3$  have room-temperature magnetic moments at 4.2  $\mu_B$  which rise to 4.7  $\mu_B$  at 373 K due to a slight increase in the amount of high-spin form relative to the low-spin form.<sup>5</sup> Figure 2 shows the far-infrared spectra of  $\text{Fe}(\text{Et}_2\text{dtc})_3$  when the temperature is raised from 328 to 372 K. As the temperature is increased, the low-spin Fe-S stretching band at 338  $\text{cm}^{-1}$  does decrease in intensity and the high-spin band at 236.4  $\text{cm}^{-1}$  increases. The ligand band at 394.6  $\text{cm}^{-1}$  remains constant in intensity but the band at 357.0  $\text{cm}^{-1}$ , which is primarily a ligand band, increases slightly in intensity.

A similar effect is observed in the  $\text{Fe}(\text{Me}_2\text{dtc})_3$  spectrum: i.e., the high-spin Fe-S stretching band at 235.0  $\text{cm}^{-1}$  and the ligand band at 362.2  $\text{cm}^{-1}$  increase slightly, while the low-spin band at 338.0  $\text{cm}^{-1}$  decreases as the temperature is increased. The low-intensity bands at 300 and 275  $\text{cm}^{-1}$  are not present

(19) B. Hutchinson, M. Hoffbauer, and J. Takemoto, *Spectrochim. Acta, Part A*, **32A**, 1785 (1976).

(20) J. Takemoto and B. Hutchinson, *Inorg. Chem.*, **12**, 705 (1973).

(21) Also in this paper  $^{54}\text{Fe}/^{57}\text{Fe}$  substitution is employed to assign an Fe-S stretching vibration in  $\text{Fe}(N\text{-Et-N-Phdtc})_3$ , a mixed-spin complex. A 15- $\text{cm}^{-1}$  shift for a band in the  $^{54}\text{Fe}$  compound at 341  $\text{cm}^{-1}$  is reported, although a maximum 7- $\text{cm}^{-1}$  shift is expected for such an absorption.

Table V. Correlation of Metal-Ligand Stretching Band Position, Electron Arrangement, and Bond Length

compd	spin arrangement	bond	length, Å	ref	metal-ligand stretching range, cm <sup>-1</sup>	ref
Fe[(pyr)dtc] <sub>3</sub>	high spin	Fe <sup>III</sup> -S	2.41	11	210-240	<i>a</i>
Fe(Et <sub>2</sub> dtc) <sub>3</sub>	low spin (79 K)	Fe <sup>III</sup> -S	2.31	12	300-340	<i>a</i>
Fe[HB(3,5-Me <sub>2</sub> -1-pz) <sub>3</sub> ] <sub>2</sub>	high spin	Fe <sup>II</sup> -N	2.17	22	200-260	19
Fe[HB(1-pz) <sub>3</sub> ] <sub>2</sub>	low spin	Fe <sup>II</sup> -N	1.97	22	395-435	19
Fe(phen) <sub>2</sub> (SCN) <sub>2</sub>	high spin (300 K)	Fe <sup>II</sup> -N(phen)	2.17	23	220-255	20
Fe(phen) <sub>2</sub> (SCN) <sub>2</sub>	low spin (100 K)	Fe <sup>II</sup> -N(phen)	2.01	23	370-380	20

<sup>a</sup> This work.

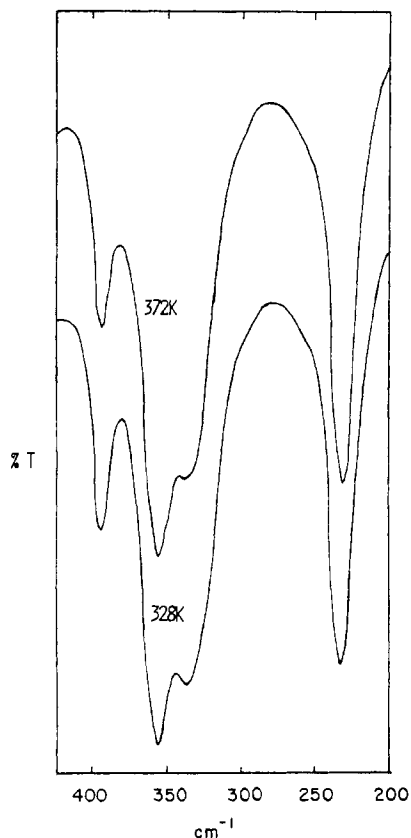


Figure 2. Infrared spectra of iron tris(diethyldithiocarbamate) at 328 and 372 K.

at 373 K. No changes in any of the band positions are noted with these temperature changes.

The results of our spectral measurements of Fe(Et<sub>2</sub>dtc)<sub>3</sub> and Fe(Me<sub>2</sub>dtc)<sub>3</sub> below room temperature are similar to those obtained previously. The results of metal isotopic substitution at low temperatures is given for these complexes in Table IV. The far-infrared spectra for stepwise temperature reduction of Fe(Me<sub>2</sub>dtc)<sub>3</sub> in the 300-400-cm<sup>-1</sup> region from 30-300 K is given in ref 7 and the 450-150-cm<sup>-1</sup> region at 30 K in ref 18. These data show that the room-temperature band at 338.0 cm<sup>-1</sup> increases in intensity as the temperature is lowered. The <sup>54</sup>Fe/<sup>57</sup>Fe isotopic shift at ~100 K for this band is 1.3 cm<sup>-1</sup>, less than the 2.5-cm<sup>-1</sup> shift at room temperature, and its minimum is at 342.2 cm<sup>-1</sup>. At 30 K the appearance of a shoulder indicates two bands are present in this envelope, probably causing the new minimum and the decrease in isotopic shift.<sup>7</sup> The high-spin Fe-S stretching band at 235.0 cm<sup>-1</sup> decreases in intensity as the temperature is lowered and is not present at 30 K.<sup>18</sup> The same is true of the ligand band at 362.2 cm<sup>-1</sup>. Two additional bands appear in the 100-K spectrum which show isotopic shifts. At this temperature, the band at 304.9 cm<sup>-1</sup> is intense enough to measure and gives an isotopic shift of 1.8 cm<sup>-1</sup>. We suggest this is possibly a low-spin Fe-S

stretching band. A new, broad band appears in the high-spin Fe-S stretching region which shows some isotopic shift. This may be a low-spin Fe-S bending band.

A similar analysis can be made for the Fe(Et<sub>2</sub>dtc)<sub>3</sub> complex as shown by the work of Sorai.<sup>14</sup> One difference is the appearance at ~175 K of a band at 320.2 cm<sup>-1</sup>. Since this band does not show any isotopic shift, it is assigned as being due to a ligand vibration. The other difference is the much smaller decrease in the intensity of the Fe-S high-spin stretching band at 235.0 cm<sup>-1</sup> compared to that of Fe-(Me<sub>2</sub>dtc)<sub>3</sub>. Also at 30 K the band about 336 cm<sup>-1</sup> splits into two bands, but isotopic comparisons were not made at this temperature.

The differences of these spectra, at room and at very low temperatures, are not unexpected in view of the X-ray crystal and differential thermal analysis data collected on Fe(Et<sub>2</sub>dtc)<sub>3</sub>. For this complex, differential thermal analysis indicates a phase transition at 125 K,<sup>14</sup> and an X-ray single-crystal study comparing structural arrangement at 297 and 79 K reveals a change in space group and in distortion from octahedral symmetry along with the average Fe-S bond distance contraction.<sup>22</sup>

Sorai has suggested that low-spin Fe-S stretching bands may appear in the 500-cm<sup>-1</sup> region on the basis of the smooth correlation of the intensity of the 552-cm<sup>-1</sup> band in Fe(Et<sub>2</sub>dtc)<sub>3</sub> and its magnetic moment value as the temperature is decreased.<sup>14</sup> Such an assignment placed the low-spin Fe-S stretch about 200 cm<sup>-1</sup> higher than the high-spin, which is a more reasonable separation than the 30-60 cm<sup>-1</sup> previously suggested. Hall also noted the effect of temperature on this 552-cm<sup>-1</sup> band but concluded that it was not a low-spin Fe-S stretching mode.<sup>18</sup> Our metal-isotope studies lead us to agree with Hall. No bands in the 400-600-cm<sup>-1</sup> region in the low-temperature spectrum of either the Fe(Et<sub>2</sub>dtc)<sub>3</sub> or Fe(Me<sub>2</sub>dtc)<sub>3</sub> show isotopic shifts. A new band does appear at 523 cm<sup>-1</sup> in Fe(Me<sub>2</sub>dtc)<sub>3</sub> at lower temperature; but it, too, shows no metal isotopic shift. The assignment of Fe-S stretching bands we have made in this study gives a reasonable separation of the high- and low-spin species also makes the low-spin Fe-S Sorai assignment unnecessary.

The correlation of the intensity of bands in the far-infrared region with the approximate concentration of the high- and low-spin form does not seem to be sufficient evidence for assigning metal-ligand stretching bands in these complexes since predominantly ligand absorptions may also show such intensity characteristics.

### Conclusion

Table V summarizes infrared and X-ray crystal structure data for three iron crossover systems. It indicates that the iron tris(dialkyldithiocarbamate) systems have Fe-S stretching bands at reasonable separations for high- and low-spin and appear in the spectral regions expected from previous studies

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of iron crossover compounds. The largest bond length change for iron crossover compounds (0.20 Å) is reflected in the largest high-spin/low-spin Fe–ligand stretching separation of  $\sim 185\text{ cm}^{-1}$  in the Fe[HB(1-pz)<sub>3</sub>]<sub>2</sub> (pz = pyrazolyl) system. A smaller decrease in bond length and change of Fe–N(phen) stretching band position occurs in Fe(phen)<sub>2</sub>(SCN)<sub>2</sub>. The Fe(III)–S bond length and stretching band positions are altered even less upon a change from high-spin to low-spin. The similarity of the three high-spin Fe–ligand stretching bands implies that the Fe(III) system does not give as favorable a

$\pi$  overlap as the Fe(II) systems in this low-spin arrangement.

**Acknowledgment.** This work was supported by the Robert A. Welch Foundation (Grant No. R-483) and the Research Council at Abilene Christian University. We wish to thank the Chemistry Department at the University of Texas at Austin for the use of their Digilab FT-IR.

**Registry No.** Fe(Et<sub>2</sub>dtp)<sub>3</sub>, 18432-76-3; Fe[(pyr)dte]<sub>3</sub>, 21288-86-8; Fe(*i*-Pr<sub>2</sub>dte)<sub>3</sub>, 54181-43-0; Fe(Et<sub>2</sub>dte)<sub>3</sub>, 13963-59-2; Fe(Me<sub>2</sub>dte)<sub>3</sub>, 14484-64-1.

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## Structure of the Gd(fod)<sub>3</sub> Adduct of [*N,N'*-Ethylenebis(acetylacetonate iminato)]nickel(II) in Solution by NMR Spin–Lattice Relaxation Studies

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Received September 23, 1980

Gd(fod)<sub>3</sub> has a pronounced effect on <sup>13</sup>C and <sup>1</sup>H NMR spin–lattice relaxation rates of [*N,N'*-ethylenebis(acetylacetonate iminato)]nickel(II) (I) in chloroform solution. A Gd(fod)<sub>3</sub>I adduct is formed which is in rapid equilibrium with its components. The Gd(III) ion is assumed to bind to both oxygens of I with normal Gd–O bond lengths, and the position of Gd(III) relative to I is determined from analysis of paramagnetic contributions to the relaxation rates of two carbon atoms. The Gd(III) ion is located at a point  $\sim 1.8\text{ Å}$  out of the plane of I. Distances from Gd(III) to the other carbon atoms and to the protons are calculated from the appropriate NMR relaxation rates. These distances are compared with those determined with the use of crystallographic data for I and by assuming that Gd(III) is located correctly by the NMR data. The agreement is within the limits of error in all cases, thus supporting assumptions made in devising the model.

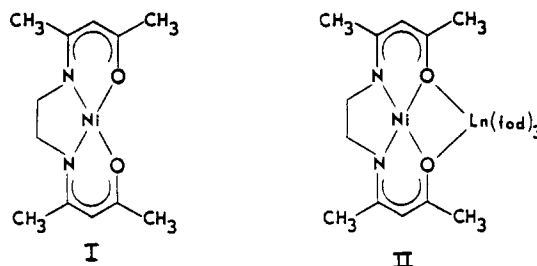
### Introduction

The theory of nuclear relaxation in the presence of paramagnetic ions was developed in the 1950's by Solomon, Bloembergen, and other,<sup>1–5</sup> and during the following two decades paramagnetic ion enhanced nuclear relaxation data has been applied numerous times to obtain structural information on enzymes in the solution phase.<sup>6–9</sup> Several comprehensive reviews of the theory and applications of this method are available.<sup>10–12</sup>

Up to the present time, there have been relatively few applications of NMR relaxation enhancement techniques to smaller molecules. Structural information has been obtained by using selected paramagnetic ions as relaxation probes for borneols,<sup>13</sup> ATP,<sup>14</sup> AMP,<sup>15</sup> histidine,<sup>16,17</sup> *N*-acetyl-3-nitro-

tyrosine,<sup>18</sup> sarcosine,<sup>19</sup> catecholamines,<sup>20</sup> an iron(III) porphyrin,<sup>21</sup> and a thiocyanate complex of Gd(III).<sup>22</sup>

A paper by Lindoy and Moody<sup>23</sup> in 1977 described interactions of the lanthanide shift reagents Eu(fod)<sub>3</sub> and Pr(fod)<sub>3</sub> (where fod is the anion of CF<sub>3</sub>CF<sub>2</sub>COCH<sub>2</sub>COC(CH<sub>3</sub>)<sub>3</sub>) with diamagnetic, planar complexes such as I. The pattern



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of observed <sup>1</sup>H and <sup>13</sup>C isotropic shifts strongly indicates that the oxygen atoms of I are bound to the lanthanide ion in a bidentate manner as shown in II. Plots of isotropic shifts vs. the mole ratio of Ln(fod)<sub>3</sub>:I show that the stoichiometry of the adduct is 1:1.

The proposed structure of the adduct is in accord with the known tendency of lanthanide ions in shift reagents to expand their coordination numbers from 6 to 8.<sup>24</sup> It is also consistent

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