The ^{19}F magnetic resonance spectrum of the mixed compound $F_5TeOXeOSeF_5$ provides for the comparison of the ionicity of the two different Xe–O ligand bonds. It is seen that the $OSeF_5$ group has slightly more covalent character and the $OTeF_5$ group slightly more ionic character compared with the related compounds A and B. This means that the first of the two canonical forms in the resonance hybrid[20] $(F_5SeOXe)^+(OTeF_5)^- \leftrightarrow (F_5SeO)^-(XeOTeF_5)^+$ is of greater importance.

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Iron(II) Complexes with Two and Three Dialkyldithiocarbamate Ligands. Mossbauer and Electronic Spectra

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A series of tris(N,N-dialkyldithiocarbamato)iron(II) complexes has been synthesized for the first time. The Mossbauer and electronic spectra of these complexes together with those of bis(N,N-dialkyldithiocarbamato)iron(II) have been measured. Small isomer shift values confirm the covalent character of the iron–sulfur bonds. The quadrupole splitting differs for six- and five-coordination; both coordination numbers occur in the bis(dimethyldithiocarbamato)iron(II) complex.

I. Introduction

Tris(N,N-dialkyldithiocarbamato)iron(III) complexes (Fe-$(R_2dtc)_3$) have been investigated thoroughly with the help of Mossbauer spectroscopy and other techniques.[1-5] Recently the iron(IV) analog $(BF_4)Fe(R_2dtc)_3$ was prepared by Pasek and Straub.[6] Pignolet, Lewis, and Holm have reported the synthesis of $Fe(R_2dtc)_2tdf$[7] and $Fe(R_2dtc)_2mnt$[8] where tdf = perfluoromethyldithiolene and mnt = maleonitriledithiolene. These complexes contain similarly a FeS_6 core. A review on this type of compound was given by Coucouvanis.[9] In this work the preparation and properties of the corresponding iron(II) complexes $(R'_4N)Fe(Et_2dtc)_3$ (R'_4N^+ is a tetraalkyl-ammonium ion) are discussed in connection with measurements on $Fe(R_2dtc)_2$ complexes.[7,10,11] These iron(II) complexes were investigated mainly by means of Mossbauer spectroscopy and electronic spectroscopy. Because of the air sensitivity of the compounds these techniques offer advantages over other experimental procedures.

II. Experimental Section

Preparation of the Complexes. The complexes discussed in this paper are very air sensitive, even when dry; hence all preparations were carried out under exclusion of air using vacuum techniques.

The bis(N,N-dialkyldithiocarbamato)iron(II) complexes (Fe(R$_2$-

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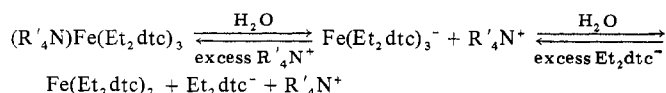(10) K. Gleu and R. Schwab, *Angew. Chem.*, 62, 320 (1950).

(11) J. P. Fackler, Jr., and D. G. Holah, *Inorg. Nucl. Chem. Lett.*, 2, 251 (1966).

dtc)$_2$ with R = methyl, ethyl, n-propyl, n-butyl, or phenyl) were prepared by mixing aqueous solutions of stoichiometric amounts of ferrous sulfate and the sodium salt of the dithiocarbamate required.[7,10] The ligand solution may also be prepared by adding CS_2 to an aqueous stirred solution of NaOH and the appropriate dialkylamine or diphenylamine. The sulfate and ligand solutions were thoroughly degassed by a repeated freezing, pumping, and thawing procedure. After mixing both solutions the suspension of the complex was deposited on a filter and flushed with previously degassed water. The washing water was collected for later analysis and the complex was dried by immersing part of the apparatus in liquid nitrogen.

The iron(II) tris(dithiocarbamate) complexes (Fe(Et$_2$dtc)$_3^-$) were prepared in the same way, but now an excess of tetraalkylammonium chloride (R'$_4$NCl, R' = butyl or ethyl) or tetraphenylphosphonium chloride (Ph$_4$PCl) was added to the ferrous sulfate solution. The purification of the tris complexes has to take place within a short time, otherwise Fe(Et$_2$dtc)$_2$ is formed. This can be observed by a change of color from brightly yellow to brown. In the final product the presence of Fe(Et$_2$dtc)$_2$ is easily revealed by its Mossbauer spectrum. On adding dithiocarbamate ligand to the reaction mixture, the tris complex can be formed again from the bis complex. The stability of the tris complexes decreases with decreasing size of the cation: (Et$_4$N)Fe(Et$_2$dtc)$_3$ transforms easily into the bis complex and attempts to prepare NaFe(Et$_2$dtc)$_3$ were unsuccessful. No evidence was found for the formation of Fe(Et$_2$dtc)$_2$Cl$^-$: (a) the Mossbauer spectra of complexes prepared with an excess of Bu$_4$NCl, Bu$_4$NBr, and Bu$_4$NI are identical, (b) the complex could also be prepared with the use of (Bu$_4$N)$_2$SO$_4$, (c) no Et$_2$dtc$^-$ has been found in the washing water if stoichiometric amounts of starting materials were used, and (d) no halogen was found in the complex and no iron–chlorine band was observed in the infrared spectrum. The products have been characterized by ir, Mossbauer, and electronic spectra and by elemental analyses. Since elemental analyses could only be carried out in the presence of air, oxidation could not be excluded.

Anal. Calcd for Fe(Me$_2$dtc)$_2$: C, 24.32; H, 4.09; N, 9.46. Found: C, 23.93; H, 3.96; N, 9.29. Calcd for Fe(Et$_2$dtc)$_2$: C, 34.06; H, 5.71; N, 7.94. Found: C, 33.67; H, 5.81; N, 7.85. Calcd for Fe(Ph$_2$dtc)$_2$: C, 57.33; H, 3.69; N, 5.13. Found: C, 55.45; H, 3.85; N, 4.81. (The agreement is further improved by comparing the experimental values with the percentages calculated for oxidation products [Fe(R$_2$dtc)$_2$]$_2$O. Calcd for R = Me: C, 23.68; H, 3.98; N, 9.21. Calcd for R = Et: C, 33.33; H, 5.59; N, 7.77. Calcd for R = Ph: C, 56.50; H, 3.64; N, 5.06.) Calcd for (Et$_4$N)Fe(Et$_2$dtc)$_3$: C, 43.79; H, 7.99; N, 8.88. Found (after oxidation): C, 41.50; H, 7.35; N, 8.66. Calcd for (Bu$_4$N)Fe(Et$_2$dtc)$_3$: C, 50.10; H, 8.95; N, 7.54. Found: C, 48.01; H, 8.62; N, 7.27. Calcd for (Ph$_4$P)Fe-

(Et$_2$dtc)$_3$: C, 55.76; H, 6.00; N, 5.00. Found: C, 53.44; H, 5.78; N, 4.93. It is seen that the ratios between the percentages calculated for the iron(II) complex and the values found for the complex after exposure to air are 1.04 on the average for all three elements The nature of the oxidation products formed and thus the amount of oxygen taken up is not known yet; the process may be rather complicated as was also observed in the formation of iron(IV) dithiocarbamates from iron(III) dithiocarbamates.[6] The iron:ligand ratio was checked by using stoichiometric amounts of starting materials and analyzing the washing water; no ferrous ions or ligand could be detected. The C, H, and N analyses were carried out on samples whose Mossbauer spectra confirmed the presence of only one species. No analyses were made of Fe(n-Pr$_2$dtc)$_2$ and Fe(n-Bu$_2$dtc)$_2$, since the close agreement of the Mossbauer parameters with those of Fe-(Et$_2$dtc)$_2$ as well as the ir data leave no doubt with regard to the formation of these complexes.

Mossbauer and Optical Measurements. Mossbauer spectra were recorded with a constant-acceleration spectrometer using an electromechanical transducer and a multichannel analyzer in the time mode. The velocity scale was calibrated using an iron-foil spectrum. For the low-temperature spectra the absorbers were mounted on a copper tube immersed in liquid nitrogen and thermally isolated with Styrofoam. With a heater the temperature could be regulated to within 1°. Absorbers were prepared in the glove box (VAC HE-43-6), where the powders were sealed in polypropylene capsules[12] and thus were protected from air. As the Mossbauer source ^{57}Co in palladium was used. The accuracy of the Mossbauer data is 0.03 mm/sec, unless stated otherwise. The electronic absorption spectra of the complexes were measured in the solid state with a Cary 14 spectrometer. Solid-state spectra were preferred since on dissolving the complexes unexpected reactions may occur. Absorbers were prepared in the glove box by mixing the complex with KBr; the mixture was placed in a die, enclosed in a plastic bag, and taken out of the box. In this way pellets could be pressed in the absence of air. Once pressed, the samples were found to be insensitive to air.

III. Results and Discussion

a. **Reaction Mechanisms.** The reversible conversion in water of the tris(dithiocarbamate) complexes into the bis complexes suggests the following equilibria in the absence of oxygen

$$(R'_4N)Fe(Et_2dtc)_3 \underset{\text{excess R}'_4N^+}{\overset{H_2O}{\rightleftharpoons}} Fe(Et_2dtc)_3^- + R'_4N^+ \underset{\text{excess Et}_2dtc^-}{\overset{H_2O}{\rightleftharpoons}}$$
$$Fe(Et_2dtc)_2 + Et_2dtc^- + R'_4N^+$$

In agreement with this proposed equilibrium the oxidation products of $(R'_4N)Fe(Et_2dtc)_3$ differ for wet oxidation and dry oxidation. The Mossbauer spectrum of the oxidation product obtained in the presence of water resembles that of the oxidation product of Fe(Et$_2$dtc)$_2$. When Fe(Et$_2$dtc)$_3^-$ complexes are oxidized in the absence of water, various observations indicate that Fe(Et$_2$dtc)$_3$ is formed: (a) on washing the oxidation product, no ligand was found in the washing water; (b) Mossbauer spectra (see Table II) and infrared spectra were identical with those of Fe(Et$_2$dtc)$_3$, including the characteristic QS dependence on the temperature;[5] (c) finally the electronic spectrum of the oxidation product was the same as the spectrum of Fe(Et$_2$dtc)$_3$, showing one spin-forbidden band at 6500 cm^{-1} (see Figure 4b and 4c).

It is interesting to compare these oxidation reactions with the oxidation process of Fe(R$_2$dtc)$_2$, which in water is oxidized slowly. If this oxidation product (QS = 1.28 mm/sec; see Table II) is recrystallized from chloroform, the QS of the compound is reduced to 0.59 mm/sec. A possible explanation is that in the first oxidation product the dimers occurring in the iron(II) complex are still present, while on recrystallization the dimers dissociate and a complex with the same elemental composition but with different geometry is formed.

b. **Iron(II) Bis(dithiocarbamate) Complexes.** Mossbauer

Table I. Mossbauer Parameters (mm/sec) of Iron(II) Dithiocarbamate, Xanthate (xn), and Diselenocarbamate (dsc) Complexes, Measured at 100°K[a]

	IS	QS		IS	QS
Fe(Me$_2$dtc)$_2$	1.19	4.10	Fe(n-Bu$_2$dtc)$_2$	1.12	4.01
	1.22	2.53	Fe(Ph$_2$dtc)$_2$	1.21	3.76
Fe(Et$_2$dtc)$_2$[b]	1.16	4.16	Fe(n-Bu(xn))$_2$	1.24	2.04
Fe(n-Pr$_2$dtc)$_2$	1.14	4.15	Fe(Et$_2$dsc)$_2$	1.09	4.06

[a] IS is given relative to Na$_2$Fe(CN)$_5$NO·2H$_2$O.   [b] See also ref 13.
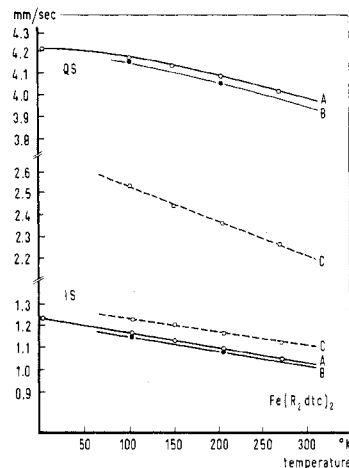
Figure 1. IS and QS as functions of temperature for (A) Fe-(Et$_2$dtc)$_2$, (B) Fe(n-Pr$_2$dtc)$_2$, and (C) the extra site of Fe(Me$_2$dtc)$_2$.

spectra were measured on bis(dithiocarbamate) complexes with five different R groups. The results are presented in Table I. In Figure 1 the temperature dependence of the Mossbauer parameters of three species is shown. X-Ray powder spectra have shown that the Fe(Et$_2$dtc)$_2$ complex occurs in the dimeric form, the iron atom being coordinated by five sulfur atoms.[11] The spin multiplicity has not been measured. In a recent paper[13] it was shown by molecular orbital calculations that the quadrupole splitting (QS) obtained for the high-spin configuration ($S = 2$) is in much better agreement with the experimental QS than the QS value calculated for the intermediate spin state ($S = 1$). The five-coordination was shown to result in four relatively closely spaced energy levels with mainly iron 3d character; the calculated energy differences between these levels are of the order of 1000 cm^{-1}. A fifth level with mainly 3d$_{xy}$ character (pointing toward the sulfur atoms) lies much higher (about 18,000 cm^{-1}). Nevertheless this level contributes significantly to the QS since due to covalency the 3d$_{xy}$ atomic orbital population is considerably larger than 1.00 (see ref 13, Table V). Thus the unusually large QS arises from the combination of five-coordination and strong covalency of the iron–ligand bonds. The observed temperature dependence of the QS suggests the spacing between the lowest levels with 3d character to be a few hundred reciprocal centimeters at most, instead of the calculated 1000 cm^{-1}.

The values of the isomer shifts (IS) are somewhat lower than for most other high-spin iron(II) compounds, for which the IS is on the average 1.4 mm/sec. This can be attributed to the considerable degree of covalency in the iron–sulfur bonds and to the five-coordination.[11] The six-coordinated iron(II) tris(dithiocarbamates) have a slightly higher IS. The temperature dependence of the IS's of the iron(II) bis(dithiocarbamates) does not show any anomalies and is explained by

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the second-order Doppler shift. For complexes with R = ethyl and n-propyl no d–d transitions in the electronic spectrum were observed, in spite of the low symmetry and in contrast with the five-coordinated iron(III) complex $Fe(Et_2dtc)_2Cl$.[13] Occasionally samples of $Fe(Me_2dtc)_2$ exhibited two broad, weak absorption bands in the near-infrared–visible region, *viz.*, at 6600 and 9400 cm^{-1}. These bands, which disappear on oxidation, are probably d–d bands corresponding with $^5E_g \leftarrow {}^5T_{2g}$ transitions; the corresponding $10Dq$ value is about 8000 cm^{-1}. The Mossbauer spectra of samples showing these electronic transitions invariably show the presence of a second quadrupole pair; see Figure 2. The relative intensity of the two Mossbauer quadrupole pairs varied with each preparation and no systematic dependence on the preparation procedure was found. Formation of $Fe(Me_2dtc)_2$-$(H_2O)_2$ is not likely on the basis of elemental analyses, which gave results as reported in the Experimental Section independent of the ratio of the two quadrupole pairs. Furthermore, heating under vacuum did not change the relative intensity of both pairs, the infrared spectra did not show any peaks that could be ascribed to monodentate dithiocarbamate ligand[14] or to thiuram disulfide, and the electronic spectrum is very similar to that observed for $Fe(R_2dtc)_3^-$, where iron is six-coordinated (see next section). These observations lead us to conclude that partly reaction to six-coordination has taken place, in agreement with the smaller QS, which is in the range of QS values normally observed for neutral high-spin six-coordinated iron(II) chelates. It is reasonable to assume that six-coordination in the dithiocarbamate complex occurs by polymerization between two or more dimeric units. In high-spin iron(II) chelates with ligands binding through oxygen or nitrogen, polymerization is very common.[15] Coordination by six sulfur atoms similar to that proposed here for the second configuration of $Fe(Me_2dtc)_2$ has been observed recently for Cu(II) in $Cu^{II}(Bu_2dtc)_2 \cdot 2Cu^{III}(Bu_2dtc)_2Cd_2Br_6$.[16] It is interesting to note that the QS and IS measured on the related iron(II) bis(n-butyl xanthate) complex, listed in Table I, also suggest six-coordination in this compound. The larger QS indicating five-coordination has never been observed in this case.

The effect of covalency of the iron–ligand bond can be investigated by replacing the sulfur atoms by selenium. Preliminary results on iron(II) bis(diselenocarbamate) (prepared from $^{57}FeCl_2$ and zinc(II) bis(diselenocarbamate) gave QS = 4.06 mm/sec and IS = 1.09 mm/sec. The large QS points to five-coordinated iron in this complex; the low IS indicates that the iron–selenium bond is even more covalent than an iron–sulfur bond.

c. **Iron(II) Tris(dithiocarbamate) Complexes.** In Table II the Mossbauer data of tris(dithiocarbamate) complexes are listed and in Figure 3 some Mossbauer spectra are shown. The IS's are indicative of high-spin complexes, and the temperature dependence of the IS's indicates the absence of spin-state equilibria in contrast with the corresponding $Fe(Et_2dtc)_3$ complexes.[2,5] Apparently in the less covalent iron(II) compounds the low-spin state is energetically unfavorable. The QS's are normal for six-coordinated high-spin iron(II). There is no relationship between QS and the size of the counterion. In the isoelectronic $Ni^{IV}(Et_2dtc)_3^+$ complex the metal site

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(15) J. L. K. F. de Vries, J. M. Trooster, and E. de Boer, to be submitted for publication.
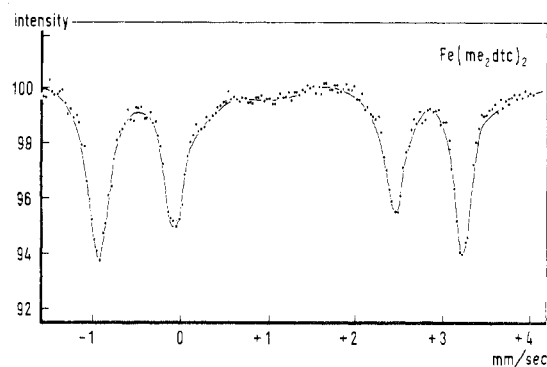(16) J. A. Cras, J. Willemse, A. W. Gal, and B. G. M. C. Hummelink-Peeters, *Recl. Trav. Chim. Pays-Bas,* **92,** 641 (1973).

Figure 2. Mossbauer spectrum of $Fe(Me_2dtc)_2$ showing two iron sites (see text), measured at 100°K.
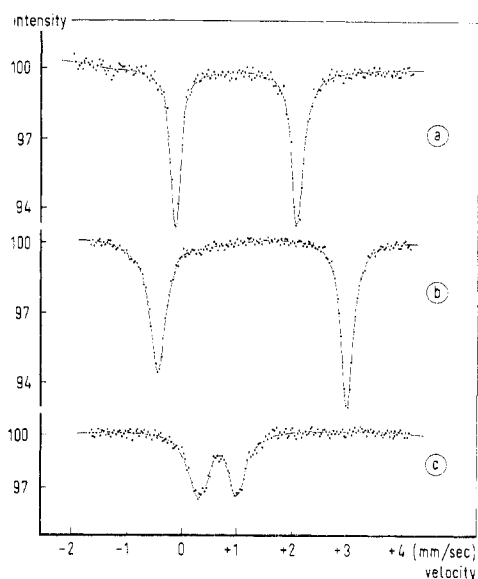
Figure 3. Mossbauer spectra of (a) $(Ph_4P)Fe(Et_2dtc)_3$, (b) (Bu_4N)-$Fe(Et_2dtc)_3$, and (c) $(Bu_4N)Fe(Et_2dtc)_3$ after oxidation, measured at 100°K.

Table II. Mossbauer Parameters of Some $Fe(Et_2dtc)_3^-$ Complexes and of Oxidation Products of Iron(II) Dithiocarbamates (mm/sec)^a

	100°K		300°K^b	
	IS	QS	IS	QS
$(Ph_4P)Fe(Et_2dtc)_3$	1.30	2.26	1.8	1.8
$(Bu_4N)Fe(Et_2dtc)_3$	1.26	3.42	1.2	3.2
$(Et_4N)Fe(Et_2dtc)_3$	1.29	3.11	1.2	2.5
$[Fe(Et_2dtc)_2]_2 + O_2{}^c$	0.68	1.28		
$[Fe(Et_2dtc)_2]_2 + O_2$ after recrystn^c	0.77	0.59		
$Fe(Et_2dtc)_3^- + O_2$ (dry)^c	0.62	0.55	0.6	0.3
$Fe(Et_2dtc)_3{}^d$	0.72	0.55	0.66	0.26

^{a} IS is given relative to $Na_2Fe(CN)_5NO \cdot 2H_2O$. ^{b} Due to the low absorption the accuracy of these parameters is equal to 0.1 mm/sec. ^{c} See text. ^{d} Reference 5.

has trigonal symmetry;[17] assuming a similar distortion in the iron complexes the splitting of the T_{2g} levels could be estimated from the temperature dependence of the QS. The following values were derived: $(Et_4N)Fe(Et_2dtc)_3$, 600 ± 150 cm^{-1}; $(Bu_4N)Fe(Et_2dtc)_3$, 800 ± 100 cm^{-1}; $(Ph_4P)Fe(Et_2-dtc)_3$, 350 ± 50 cm^{-1}. It should be pointed out that these large QS's and the corresponding T_{2g} splittings do not necessarily imply large deviations from octahedral symmetry. For example, the QS's in $(R_4N)_2FeCl_4$ complexes reveal a devia-

(17) A. Ardeef, J. P. Fackler, Jr., and R. G. Fisher, Jr., *J. Amer. Chem. Soc.,* **92,** 6972 (1970).

tion from tetrahedral symmetry that has not been observed in X-ray analysis; in this case the calculated splittings of the 3d orbitals are of the same order as found above for (Fe-(Et$_2$dtc)$_3$)$^-$.[18] Another example is Fe(H$_2$O)$_6$SiF$_6$, for which the large QS of 3.7 mm/sec is a consequence of an elongation of about 0.04 Å along a trigonal axis of the oxygen octahedron.[19] The Fe(Et$_2$dtc)$_3^-$ complexes show very clear electronic spectra in the 4000-13,000 cm^{-1} range, which are almost independent of the nature of the counterion in the complex. A typical spectrum is shown in Figura 4a. The intensity and width of the bands and the change of the spectrum on oxidation are taken as evidence that these bands correspond to d-d transitions. By using a Du Pont E 310 curve resolver the band positions were determined to be 7100 ± 400 and 8300 ± 300 cm^{-1}; the line width is about 2000 cm^{-1}. We assume as in the case of the second Fe(Me$_2$dtc)$_2$ species that these two bands are the two components of the $^5E_g \leftarrow {}^5T_{2g}$ transition; the relatively small splitting seems to confirm the high symmetry of the Fe(Et$_2$dtc)$_3^-$ ion. The 10Dq value thus found for the Et$_2$dtc$^-$ ligand is about 7700 cm^{-1}. This value seems to be somewhat low when compared to the 10Dq value of about 8800 cm^{-1} derived for F$^-$ from the d-d spectrum of FeF$_2$;[20] Et$_2$dtc$^-$ and F$^-$ occupy neighboring positions in the spectrochemical series. However the observed value agrees with the 10Dq value derived from the spectrum of the Fe-(Me$_2$dtc)$_2$ (*vide supra*). The much larger 10Dq of Me$_2$dtc$^-$ as estimated for Fe^{III}(Me$_2$dtc)$_3$ (about 12,800 cm^{-1})^2 is in agreement with the more covalent character of iron(III) compounds as compared to iron(II) compounds. Ir spectra of (R$'_4$N)Fe(Et$_2$dtc)$_3$ measured in KBr disks resemble closely those of Fe(Et$_2$dtc)$_3$. There is possibly a small shift in the frequency of the C-N band (Fe(Et$_2$dtc)$_3$, 1483 ± 3 cm^{-1}; (R$'_4$N)Fe(Et$_2$dtc)$_3$, 1478 ± 3 cm^{-1}), much smaller than the difference observed between Fe(Et$_2$dtc)$_3$ and (BF$_4$)Fe(Et$_2$-dtc)$_3$.[6]

IV. Summary

The present results show that tris(dithiocarbamate) complexes of iron(IV) and iron(III) can be extended to iron(II). In general a decrease of the oxidation state of the metal lowers the degree of covalency. In accordance with this the iron(IV) complexes are in the low-spin state,[6] and the iron(III) complexes may occur in high-spin as well as in low-spin states,[2] while the experimental data (IS and electronic spectrum) for the iron(II) complex point to a high-spin state. The IS of Fe(R$_2$dtc)$_3^-$ is smaller than the IS of tris(acetylacetonato)iron(II) where the iron is coordinated by six oxygen atoms (IS = 1.41 mm/sec at 100°K),[15] which reflects the increase of covalency on going from an iron-oxygen to an

(18) P. R. Edwards, C. E. Johnson, and R. J. P. Williams, *J. Chem. Phys.*, 47, 2074 (1967).

(19) W. C. Hamilton, *Acta Crystallogr.*, 15, 353 (1962).
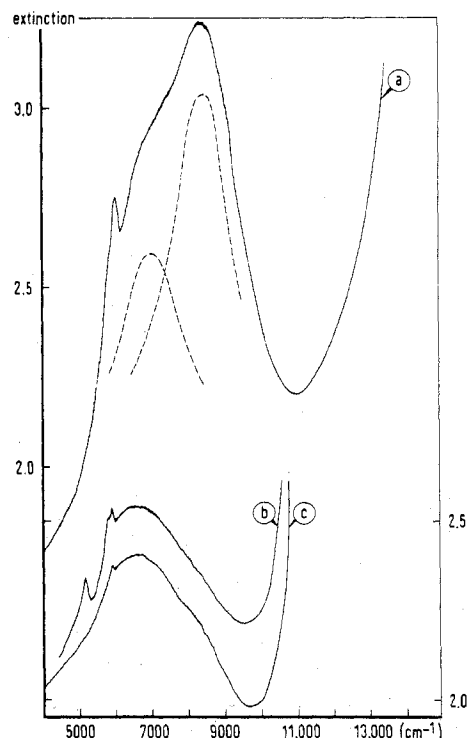
(20) G. D. Jones, *Phys. Rev.*, 155, 259 (1967).

Figure 4. Electronic spectra of (a) (Ph$_4$P)Fe(Et$_2$dtc)$_3$, (b) (Ph$_4$P)-Fe(Et$_2$dtc)$_3$ after oxidation in the absence of water, and (c) Fe-(Et$_2$dtc)$_3$. All spectra were measured on KBr disks.

iron-sulfur bond. In most high-spin iron(II) complexes and chelates the iron is surrounded by oxygen atoms with a coordination number of 6. Because of the increased covalency in complexes with sulfur-binding ligands five-coordination is observed in bis(dithiocarbamate) complexes, while in the iron(II) bis(dimethyldithiocarbamate) both five- and six-coordination can occur. The 10Dq value of R$_2$dtc$^-$ was found to be 8000 cm^{-1}, which is considerably smaller than the value for iron(III) complexes, as expected.