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

J. L. K. F. de VRIES, J. M. TROOSTER, and E. de BOER*

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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(dimethylthiocarbamato)iron(II) complex.

I. Introduction

Tris(\(N, N\)-dialkyldithiocarbamato)iron(III) complexes (Fe(\(R_2\)dtc)\(_3\)) have been investigated thoroughly with the help of Mossbauer spectroscopy and other techniques.\(^4\) Recently the iron(IV) analog (BF\(_4\))Fe(\(R_2\)dtc)\(_3\) was prepared by Pasek and Straub.\(^6\) Pignolet, Lewis, and Holm have reported the synthesis of Fe(\(R_2\)dtc)\(_2\)tdf\(^7\) and Fe(\(R_2\)dtc)\(_2\)mnt\(^8\) where tdf = perfluoromethylidithiolene and mnt = maleonitriledithiolene. These complexes contain similarly a FeS\(_2\) 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 (\(R'4\)N)Fe(\(Et_2\)dtc)\(_3\) (\(R'4\)N\(^+\) is a tetraalkylammonium ion) are discussed in connection with measurements on Fe(\(R_2\)dtc)\(_2\) 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.

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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.

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

| Fe(Me₂dtc)₂ | 1.19 | 4.10 | Fe(n-Bu₂dtc) | 1.16 |
| Fe(Ph₂dtc)₂ | 1.22 | 2.53 | Fe(n-Bu₂dtc) | 1.14 |
| Fe(n-Bt₂dtc)₂ | 1.16 | 4.16 | Fe(n-Bu₂(xn)) | 1.14 |
| Fe(n-Bt₂dtc)₂ | 1.14 | 4.15 | Fe(Et₂dtc) | 1.16 |

* IS is given relative to Na₂Fe(CN)₆NO·2H₂O.  
* See Table II.

Figure 1. IS and QS as functions of temperature for (Et₂dtc), (B) Fe(n-Pr₂dtc)₂, and (C) the extra site of Fe(Et₂dtc)₂ complexes were measured on bis(dithiocarbamate) 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. Powder spectra have shown that the Fe(Et₂dtc)₂ cures in the dimeric form, the iron atom being covalent to five sulfur atoms. The spin multiplicity has been measured. In a recent paper 13 it was shown by orbital calculations that the quadrupole splitting for the high-spin configuration (S = 2) is in agreement with the experimental QS than the calculated for the intermediate spin state (S = 1). A high-spin state is shown to result in four relatively high energy levels with mainly iron 3d character; the energy differences between these levels are of the order of 1000 cm⁻¹. A fifth level with mainly 3dₓᵧ character toward the sulfur atoms) lies much higher (1800 cm⁻¹). Nevertheless this level contributes significantly the QS since due to covalency the 3dₓᵧ atomic energy level is considerably larger than 1.00 (see ref 13). Thus the unusually large QS arises from the covalent orbitals in the coordination and strong covalency of the iron-sulfur bonds. The observed temperature dependence suggests the spacing between the lowest levels to be a few hundred reciprocal centimeter instead of the calculated 1000 cm⁻¹. The values of the isomer shifts (IS) are somewhat smaller than for most other high-spin iron(II) compounds. 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.

The Mossbauer spectra were identical with those of Fe(Et₂dtc)₂, including the characteristic QS dependence on the temperature, as the temperature dependence of the IS's of the iron(II) complex is shown in Figure 1. Figure 1 shows the temperature dependence of the IS and the QS of Fe(Et₂dtc)₂.

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the second-order Doppler shift. For complexes with \( R = \text{ethyl} \) 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 \( \text{Fe(Et}_2\text{dtc})_2\text{Cl} \). Occasionally samples of \( \text{Fe(Me}_2\text{dtc})_2 \) 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 \( \text{S}_{\text{Eg}} \rightarrow \text{T}_{\text{2g}} \) 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 \( \text{Fe(Me}_2\text{dtc})_2 \cdot \text{H}_2\text{O} \) 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 or to thiuram disulfide, and the electronic spectrum is very similar to that observed for \( \text{Fe(R}_2\text{dtc})_3 \), 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. Coordination by six sulfur atoms similar to that proposed here for the second configuration of \( \text{Fe(Me}_2\text{dtc})_2 \) has been observed recently for \( \text{Cu(II)} \) in \( \text{Cu(II)dtc}_2 \cdot 2\text{Cu(II)dtc}_2 \cdot \text{CuBr}_2 \). 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 \( \text{FeCl}_2 \) 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 \( \text{Fe(Et}_2\text{dtc})_3 \) complexes. 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 \( \text{Ni(II)dtc}_3 \) complex the metal site has trigonal symmetry; assuming a similar distortion the complexes the splitting of the \( T_{2g} \) levels would be attributed from the temperature dependence of the Q-values were derived: \( \text{Fe(Et}_2\text{dtc})_3 \), 6 cm\(^{-1}\); \( \text{Bu}_4\text{NFe(Et}_2\text{dtc})_3 \), 750 ± 100 cm\(^{-1}\); \( \text{Ph}_4\text{PFe(Et}_2\text{dtc})_3 \), 350 ± 50 cm\(^{-1}\). It should be pointed out that large QS’s and the corresponding \( T_{2g} \) splittings do not imply large deviations from octahedral symmetry.
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 \((\text{Fe-}(\text{Et}_2\text{dtc}))_3^-\). Another example is \(\text{Fe}(\text{H}_2\text{O})_6\text{SiF}_6\), 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. The \(\text{Fe}(\text{Et}_2\text{dtc})_3^-\) 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 Figure 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 \(7100 \pm 400\) and \(8300 \pm 300\) cm\(^{-1}\); the line width is about 2000 cm\(^{-1}\). We assume as in the case of the second \(\text{Fe}(\text{Me}_2\text{dtc})_2\) species that these two bands are the two components of the \(^5\text{E}_g \rightarrow ^5\text{T}_2\) transition; the relatively small splitting seems to confirm the high symmetry of the \(\text{Fe}(\text{Et}_2\text{dtc})_3^-\) ion. The \(\Delta Dq\) value thus found for the \(\text{Et}_2\text{dtc}^-\) ligand is about 7700 cm\(^{-1}\). This value seems to be somewhat low when compared to the \(\Delta Dq\) value of about 8800 cm\(^{-1}\) derived for \(\text{F}^\text{-}\) from the d-d spectrum of \(\text{FeF}_2\). \(\text{Et}_2\text{dtc}^-\) and \(\text{F}^-\) occupy neighboring positions in the spectrochemical series. However the observed value agrees with the \(\Delta Dq\) value derived from the spectrum of the \(\text{Fe}(\text{Me}_2\text{dtc})_2\) (\textit{vide supra}). The much larger \(\Delta Dq\) of \(\text{Me}_2\text{dtc}^-\) as estimated for \(\text{Fe}^\text{III}(\text{Me}_2\text{dtc})_3\) (about 12,800 cm\(^{-1}\)) is in agreement with the more covalent character of iron(III) compounds as compared to iron(II) compounds. It spectra of \((\text{R}_4^\text{N})\text{Fe}(\text{Et}_2\text{dtc})_3\) measured in KBr disks resemble closely those of \(\text{Fe}(\text{Et}_2\text{dtc})_3\). There is possibly a small shift in the frequency of the C-N bond (\(\text{Fe}(\text{Et}_2\text{dtc})_3\), 1483 ± 3 cm\(^{-1}\); \((\text{R}_4^\text{N})\text{Fe}(\text{Et}_2\text{dtc})_3\), 1478 ± 3 cm\(^{-1}\)), much smaller than the difference observed between \(\text{Fe}(\text{Et}_2\text{dtc})_3\) and \((\text{BF}_4)\text{Fe}(\text{Et}_2\text{dtc})_3\).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, and the iron(III) complexes may occur in high-spin as well as in low-spin states, while the experimental data (IS and electronic spectrum) for the iron(II) complex point to a high-spin state. The IS of \(\text{Fe}(\text{R}_2\text{dtc})_3\) is smaller than the IS of tris(acetyl-acetonato)iron(II) where the iron is coordinated by six oxygen atoms (IS = 1.41 mm/sec at 100°K), which reflects the increase of covalency on going from an iron-oxygen to an iron-sulfur bond. In most high-spin iron(II) complexes the iron is surrounded by oxygen atoms in an octahedral coordination number of 6. Because of the increase in complexes with sulfur-binding ligands five-coordinated iron(II) bis(dimethylthiocarbamate) complexes, \(\text{Fe}(\text{R}_2\text{dtc})_2\) (\(\text{R}_2\text{dtc}^-\)), chelates the iron by one dithiocarbamate ligand and the second 

\[\text{Fe}(\text{R}_2\text{dtc})_2, 41367-62-8; \text{Fe}(\text{Et}_2\text{dtc})_2, 41429-87-7; \text{Fe}(\text{n-Pr}_2\text{dtc})_2, 41444-80-8; \text{Fe}(\text{n-Bu}_2\text{dtc})_2, 41371-79-9; \text{Fe}(\text{Et}_2\text{dtc})_2, 41371-76-0; \text{Fe}(\text{Et}_2\text{dtc})_2, 41371-78-2.\]

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Registry No. \(\text{Fe}(\text{Me}_2\text{dtc})_2, 41367-62-8; \text{Fe}(\text{Et}_2\text{dtc})_2, 41367-64-0; \text{Fe}(\text{n-Pr}_2\text{dtc})_2, 41429-87-7; \text{Fe}(\text{n-Bu}_2\text{dtc})_2, 41444-80-8; \text{Fe}(\text{n-Bu}_2\text{dtc})_2, 41371-79-9; \text{Fe}(\text{Et}_2\text{dtc})_2, 41371-76-0; \text{(Bu}_4\text{N})\text{Fe}(\text{Et}_2\text{dtc})_3, 41371-78-2.\)