Iron(II) Complexes with Two and Three Dialkylthiocarbamate 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-configuration; both coordination numbers occur in the bis(dimethylthiocarbamato)iron(II) complex.

I. Introduction

Tris(N,N-dialkyldithiocarbamato)iron(III) complexes (Fe(R2dtc)3) have been investigated thoroughly with the help of Mossbauer spectrosopy and other techniques.1-5 Recently the iron(IV) analog (BF4)Fe(R2dtc)3 was prepared by Pasek and Straub.6 Pignolet, Lewis, and Holm have reported the synthesis of Fe(R2dtc)2tdf7 and Fe(R2dtc)2mnt8 where tdf = perfluoromethyldithiolene and mnt = maleonitriledithiolene. These complexes contain similarly a FeS5 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(Et2dtc)3 (R' = methyl, ethyl, n-propyl, -butyl, or phenylamine) are discussed in connection with measurements on Fe(R2dtc)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(R2dtc)2) with R = methyl, ethyl, n-propyl, n-butyl, or phenylamine were prepared by mixing aqueous solutions of stoichiometric amounts of FeCl2·4H2O, NaH2PO4, and NaN3. The sulfate and ligand solutions were then slowly added to the ferrous sulfate solution, and NaOH was added to adjust the pH. The reaction mixture was then filtered, rinsed, and then carefully washed with water. The complexes were then dried in vacuum.

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Iron(II)-Dialkyldithiocarbamate Complexes

Iron(II)-dithiocarbamate, xanthate (xn), and diselenocarbamate complexes, measured at 100°K.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>IS</th>
<th>QS</th>
</tr>
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<tbody>
<tr>
<td>Fe(Me₂dtc)₃</td>
<td>1.19</td>
<td>4.10</td>
</tr>
<tr>
<td>Fe(n-Bu₂dtc)₂</td>
<td>1.16</td>
<td>4.16</td>
</tr>
<tr>
<td>Fe(n-Pr₂dtc)₂</td>
<td>1.14</td>
<td>4.15</td>
</tr>
<tr>
<td>Fe(n-Pr₄dtc)₂</td>
<td>1.22</td>
<td>2.53</td>
</tr>
<tr>
<td>Fe(n-Bu(xn))</td>
<td>1.16</td>
<td>4.16</td>
</tr>
<tr>
<td>Fe(n-Bu₂dtc)</td>
<td>1.14</td>
<td>4.15</td>
</tr>
</tbody>
</table>

Figure 1. IS and QS as functions of temperature for (Et₂dtc)₃, (B) Fe(n-Pr₂dtc)₂, and (C) the extra site of Fe₃O₄.

In Table I the temperature dependence of the IS’s of the iron(II) complexes is shown. In Figure 1 the temperature dependence of the IS’s of the iron(II) complexes is shown. In Figure 1 the temperature dependence of the IS’s of the iron(II) complexes is shown. In Figure 1 the temperature dependence of the IS’s of the iron(II) complexes is shown.

The reversible conversion in water of the tris(dithiocarbamate) complexes into the bis complexes suggests the following equilibria in the absence of oxygen:

\[(R_4'N)Fe(Et₂dtc)₅\] + \(\text{H₂O}\) \[\rightarrow\] Fe(Et₂dtc)₅ + \(R_4'N\) + \(\text{H₂O}\)

In agreement with this proposed equilibrium the oxidation products of \((R_4'N)Fe(Et₂dtc)₅\) differ for wet and dry oxidation. The Mössbauer spectrum of the oxidation product obtained in the presence of water resembles that of the oxidation product of Fe(Et₂dtc)₃. When Fe(Et₂dtc)₅ - complexes are oxidized in the absence of water, various observations indicate that Fe(Et₂dtc)₅ is formed: (a) on washing the oxidation product, no ligand was found in the washing water; (b) Mössbauer spectra (see Table II) and infrared spectra were identical with those of Fe(Et₂dtc)₃, including the characteristic QS dependence on the temperature; (c) finally the electronic spectrum of the oxidation product was the same as the spectrum of Fe(Et₂dtc)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(R₂dtc)₂, which in water is oxidized slowly. If this oxidation product (QS = 1.04 mm/sec, see Table II) is recrystallized from chloroform, the QS of the complex is the same as the spectrum of Fe(Et₂dtc)₃, showing one spin-forbidden band at 6500 cm⁻¹ (see Figure 4b and 4c).

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. 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 in samples whose Mössbauer spectra confirmed the presence of only one species. No analyses were made of Fe(n-Pr₂dtc)₃ and Fe(n-Bu₂dtc)₃, since the close agreement of the Mössbauer parameters with those of Fe(Et₂dtc)₃, as well as the IR data leave no doubt with regard to the formation of these complexes.

Mössbauer and Optical Measurements. Mössbauer spectra were recorded with a constant-acceleration spectrometer using an electro-mechanical 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°C. Absorbers were prepared in the glove box (VAC HE-43-6), where the powders were sealed in polypropylene capsules and thus were protected from air. As the Mössbauer source ⁵⁷Co in palladium was used. The accuracy of the Mössbauer 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:

\[(R_4'N)Fe(Et₂dtc)₅\] + \(\text{H₂O}\) \[\rightarrow\] Fe(Et₂dtc)₅ + \(R_4'N\) + \(\text{H₂O}\)

In agreement with this proposed equilibrium the oxidation products of \((R_4'N)Fe(Et₂dtc)₅\) differ for wet and dry oxidation. The Mössbauer spectrum of the oxidation product obtained in the presence of water resembles that of the oxidation product of Fe(Et₂dtc)₃. When Fe(Et₂dtc)₅ - complexes are oxidized in the absence of water, various observations indicate that Fe(Et₂dtc)₅ is formed: (a) on washing the oxidation product, no ligand was found in the washing water; (b) Mössbauer spectra (see Table II) and infrared spectra were identical with those of Fe(Et₂dtc)₃, including the characteristic QS dependence on the temperature; (c) finally the electronic spectrum of the oxidation product was the same as the spectrum of Fe(Et₂dtc)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(R₂dtc)₂, which in water is oxidized slowly. If this oxidation product (QS = 1.04 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.
the second-order Doppler shift. For complexes with \( R = \mathrm{ethyl} \) 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 \( \text{Fe(Et}_2\text{dtc)}_2\text{Cl}. \)\(^{13}\) Occasionally samples of \( \text{Fe(Me}_2\text{dtc)}_2\text{Cl} \) 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 \( ^5\text{E}_g \rightarrow ^5\text{T}_{2g} \) transitions; the corresponding \( 10\text{D}_q \) 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 \( \text{Fe(Me}_2\text{dtc)}_2\text{(H}_2\text{O)}_2 \) 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 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 \( \text{QS} \), which is in the range of \( \text{QS} \) 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 dimetric 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 \( \text{Fe(Me}_2\text{dtc)}_2\text{Cl} \) has been observed recently for \( \text{Cu(II) in Cun(Bu}_2\text{dtc)}_2 \text{-2Cun(Bu}_2\text{dtc)}_2\text{Cd}_2\text{Br}_6. \)\(^{16}\) It is interesting to note that the \( \text{QS} \) and \( \text{IS} \) measured on the related iron(II) bis(n-butyl xanthate) complex, listed in Table I, also suggest six-coordination in this compound. The larger \( \text{QS} \) 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 \( ^{57}\text{FeCl}_3 \) and zinc(II) bis(diselenocarbamate) gave \( \text{QS} = 4.06 \text{mm/sec} \) and \( \text{IS} = 1.09 \text{mm/sec}. \) The large \( \text{QS} \) points to five-coordinated iron in this complex; the low \( \text{IS} \) 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 \( \text{IS} \)'s are indicative of high-spin complexes, and the temperature dependence of the \( \text{IS} \)'s indicates the absence of spin-state equilibria in contrast with the corresponding \( \text{Fe(Et}_2\text{dtc)}_3 \) complexes.\(^{2,5}\) Apparently in the less covalent iron(II) complexes the low-spin state is energetically unfavorable. The \( \text{QS} \)'s are normal for six-coordinated high-spin iron(II). There is no relationship between \( \text{QS} \) and the size of the counterion. In the isoelectronic \( \text{Ni}^{II}(\text{Et}_2\text{dtc)}_3 \) complex the metal site has trigonal symmetry;\(^{17}\) assuming a similar distortion the complexes the splitting of the \( \text{T}_{2g} \) levels calculated from the temperature dependence of the \( \text{QS} \) values were derived: \( (\text{Et}_4\text{N})\text{Fe(Et}_2\text{dtc)}_3 \), \( 100 \pm 10 \text{cm}^{-1}; (\text{Bu}_4\text{N})\text{Fe(Et}_2\text{dtc)}_3 \), \( 350 \pm 50 \text{cm}^{-1}; (\text{Ph}_4\text{P})\text{dtc)}_3 \), \( 350 \pm 50 \text{cm}^{-1}. \) It should be pointed out that the large \( \text{QS} \)'s and the corresponding \( \text{T}_{2g} \) splittings do not imply large deviations from octahedral symmetry.

\[ IS = \text{mm/sec, } QS = \text{mm/sec. } a \text{ See text. } b \text{ See Reference 5.} \]

![Figure 2. Mossbauer spectrum of Fe(Me2dtc)2 showing two quadrupole pairs.](image)

![Figure 3. Mossbauer spectra of (a) (Ph4P)Fe(Et2dtc)3, (b) Fe(Et2dtc)2, and (c) (Bu4N)Fe(Et2dtc)3 after oxidation, measured at 100°K.](image)

Table II. Mossbauer Parameters of Some Fe(Et2dtc)3+ C and of Oxidation Products of Iron(II) Dithiocarbamates (\( \text{Mossbauer Parameters of Some Fe(Et2dtc)3+ C and of Oxidation Products of Iron(II) Dithiocarbamates (100°K)} \)

<table>
<thead>
<tr>
<th>Compound</th>
<th>IS</th>
<th>QS</th>
<th>IS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ph4P)Fe(Et2dtc)3</td>
<td>1.30</td>
<td>2.26</td>
<td>1.8</td>
</tr>
<tr>
<td>(Bu4N)Fe(Et2dtc)3</td>
<td>1.26</td>
<td>3.42</td>
<td>1.2</td>
</tr>
<tr>
<td>(Et4N)Fe(Et2dtc)3</td>
<td>1.29</td>
<td>3.11</td>
<td>1.1</td>
</tr>
<tr>
<td>[Fe(Et2dtc)3]2 + O2</td>
<td>0.68</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>(Fe(Et2dtc)3)2 + O2</td>
<td>0.77</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>after recrystallization</td>
<td>0.62</td>
<td>0.55</td>
<td>0.6</td>
</tr>
<tr>
<td>Fe(Et2dtc)3 + O2 (dry)</td>
<td>0.72</td>
<td>0.55</td>
<td>0.66</td>
</tr>
<tr>
<td>Fe(Et2dtc)3</td>
<td>1.30</td>
<td>2.26</td>
<td>1.8</td>
</tr>
</tbody>
</table>

a IS is given relative to Na2Fe(CN)5N02H2O. b Due to absorption the accuracy of these parameters is equal to 0. c See text. d Reference 5.
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-Fe-Fe)3−.18 Another example is Fe(H2O)6SiF6, 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(Fe-Fe-Fe)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 ± 400 and 8300 ± 300 cm−1; the line width is about 2000 cm−1. We assume as in the case of the second Fe(Me2dtc)2 species that these two bands are the two components of the 5Eg ← 5T2g transition; the relatively small splitting seems to confirm the high symmetry of the Fe(Fe-Fe-Fe)3− ion. The 10Dq value thus found for the Fe(Fe-Fe-Fe)3− 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 FeF2,20 but the Fe(Fe-Fe-Fe)3− 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(Fe-Fe-Fe)3− (vide supra). The much larger 10Dq of Me2dtc− as estimated for FeIII(Me2dtc)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′4N)Fe(Fe-Fe-Fe)3− measured in KBr disks resemble closely those of Fe(Fe-Fe-Fe)3−. There is possibly a small shift in the frequency of the C-N band (Fe(Fe-Fe-Fe)3−, 1483 ± 3 cm−1; (R′4N)Fe(Fe-Fe-Fe)3−, 1478 ± 3 cm−1), much smaller than the difference observed between Fe(Fe-Fe-Fe)3− and (BF4)Fe(Fe-Fe-Fe)3−.2

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,2 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(Fe-Fe-Fe)3− is smaller than the IS of iron(II) bis(dimethyldithiocarbamate) complex, which reflects the increase of covalency on going from an iron-oxoxygen to an iron-sulfur bond. In most high-spin iron(II) chelates the iron is surrounded by oxygen atom coordination number of 6. Because of the increase in complexes with sulfur-binding ligands five-coordination is observed in bis(dithiocarbamate) complexes, with iron(II) bis(dimethyldithiocarbamate) both five-coordination can occur. The 10Dq value of Fe2+ found to be 8000 cm−1, which is considerably the value for iron(III) complexes, as expected.

Acknowledgment. We wish to thank Dr. J. W. Schley for suggesting the preparation of the tris(dithiocarbamate) complexes and Mr. J. H. M. Gruyters for his cooperation in the experiments reported. The assistance of Miss M. C. van der Wal in the preparation of the experimental part of the work is gratefully acknowledged.

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Registry No. Fe(Me2dtc)2, 41367-62-8; Fe(Et2dtc)2, 41367-64-0; Fe(n-Pr2dtc)2, 41429-87-7; Fe(n-Bu2dtc)2, 41444-80-8; Fe(n-Bu2dtc)2, 41371-75-9; Fe(Fe-Fe-Fe)3−, 41371-76-0; (Bu4N)Fe(Fe-Fe-Fe)3−, 41371-78-2.

Figure 4. Electronic spectra of (a) (Ph4P)Fe(Fe-Fe-Fe)3−, (b) after oxidation in the absence of water, (Et2dtc)3−, (c) after oxidation in the absence of water, and (d) (Et2dtc)3−. All spectra were measured on KBr disks.