Iron(II) Complexes with Two and Three Dialkylidithiocarbamate Ligands.

Mossbauer and Electronic Spectra

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Received February 5, 1973

A series of bis(N,N-dialkylidithiocarbamato)iron(II) complexes have been synthesized for the first time. The Mossbauer and electronic spectra of these complexes together with those of bis(N,N-dialkylidithiocarbamato)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(dimethylidithiocarbamato)iron(II) complex.

I. Introduction

Tris(N,N-dialkylidithiocarbamato)iron(III) complexes (Fe(R2dtc)3) have been investigated thoroughly with the help of Mossbauer spectroscopy 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 = perfluoromethylidithiolene and mnt = maleonitriledithiolene. These complexes contain similarly a FeS6 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 (R4N)Fe(Et2dtc)3 (R' = methyl, ethyl, n-propyl, n-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-dialkylidithiocarbamato)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 NaFe(Et2dtc)2 and the sodium salt of the dithiocarbamate ligand. The iron(II) sulfate solutions were gassed by a repeated freezing, pumping, and thawing procedure and the complex was collected for later analysis and the complex was washed with previously degassed water. By immersing part of the apparatus in liquid nitrogen, purification of the tris complexes has to take place with air-purged water if stoichiometric amounts of starting iron(II) sulfate and the sodium salt of the dithiocarbamate were used, and (d) no halogen was found in the complex; (a) the iron–chlorine band was observed in the infrared spectrum, (b) the washing water if stoichiometric amounts of starting iron(II) sulfate and the sodium salt of the dithiocarbamate were used, and (d) no halogen was found in the complex; (a) the iron–chlorine band was observed in the infrared spectrum, (b) the washing water if stoichiometric amounts of starting iron(II) sulfate and the sodium salt of the dithiocarbamate were used, and (d) no halogen was found in the complex; (a) the iron–chlorine band was observed in the infrared spectrum, (b) the washing water if stoichiometric amounts of starting iron(II) sulfate and the sodium salt of the dithiocarbamate were used, and (d) no halogen was found in the complex.

The iron(II) tris(dithiocarbamate) complexes (Fe(Et2dtc)3) have been characterized by infrared, Mossbauer, and electronic measurements. Since elemental analyses could not be carried out in the presence of air, oxidation could not be avoided. Anal. Calcd for Fe(Me2dtc)3: C, 24.32; H, 4.09; N, 4.81. Found: C, 23.85; 8, 3.31; N, 6.18. The agreement is further improved by comparison of experimental values with the percentages calculated for the elements. Contribution from the Department of Physical Chemistry, University of Nijmegen, Nijmegen, The Netherlands.
Iron(II)-Dialkyldithiocarbamate Complexes

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

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(R_4N)Fe(Et_2dtc) + Et_2dtc^- + R_4N^+ \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 Mössbauer spectrum of the oxidation product obtained in the presence of water resembles that of the oxidation product of \(Fe(Et_2dtc)_2\). When \(Fe(Et_2dtc)_3\) complexes are oxidized in the absence of water, various observations indicate that \(Fe(Et_2dtc)_3\) 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 \(Fe(Et_2dtc)_3\), including the characteristic QS dependence on the temperature; (c) finally the electronic spectrum of the oxidation product was the same as the spectrum of \(Fe(Et_2dtc)_3\), 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 \(Fe(R_2dtc)_2\), 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) Dithiocarbamate Complexes. Mössbauer...
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 $5\text{Eg} \rightarrow 5\text{T}_{2g}$ 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 thuram disulfide, and the electronic spectrum is very similar to that observed for $\text{Fe(R}_2\text{dtc)}_3^{2+}$, 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 $\text{Q}_S$, which is in the range of $\text{Q}_S$ 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 $\text{Cu(FBu}_2\text{dtc)}_2 \cdot 2\text{Cu(Bu}_2\text{dtc)}_2 \cdot 2\text{Bu}_2\text{Br}$. It is interesting to note that the $\text{Q}_S$ 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 $\text{Q}_S$ 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 $\text{Q}_S = 4.06$ mm/sec and $\text{IS} = 1.09$ mm/sec. The large $\text{Q}_S$ 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. Apparently in the less covalent iron(II) compounds the low-spin state is energetically unfavorable. The $\text{Q}_S$'s are normal for six-coordinated high-spin iron(II). There is no relationship between $\text{Q}_S$ and the size of the counterion. In the isoelectronic Ni$^{IV}(\text{Et}_2\text{dtc})_3$ complex the metal site has trigonal symmetry; assuming a similar distorted iron complexes the splitting of the $\text{T}_{2g}$ levels calculated from the temperature dependence of the $\text{Q}_S$-giving values were derived: ($\text{Et}_4\text{N})\text{Fe(Et}_2\text{dtc)}_3$, $630 \pm 50$ cm$^{-1}$; ($\text{Bu}_4\text{N})\text{Fe(Et}_2\text{dtc)}_3$, $800 \pm 100$ cm$^{-1}$; ($\text{Ph}_4\text{P})\text{dtc}$, $350 \pm 50$ cm$^{-1}$. It should be pointed out that large $\text{Q}_S$'s and the corresponding $\text{T}_{2g}$ 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 (Fe-(Et₂dtc)₃). 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. The Fe(Et₂dtc)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 5E₉⁻⁻→5T₂₉ transition; the relatively small splitting seems to confirm the high symmetry of the Fe(Et₂dtc)₃⁻ ion. The 10Dq value thus found for the Et₂dtc⁻ 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, as estimated for Fe(III) and F⁻ occupying neighboring positions in the spectrochemical series. However the observed value agrees with the 10Dq value derived from the spectrum of the Fe(II) complexes (vide supra). The much larger 10Dq of Me₂dtc⁻ as estimated for Fe(III) and F⁻ (about 10,000 cm⁻¹) is in agreement with the more covalent character of iron(III) compounds as compared to iron(II) compounds. Its spectra of (R₄N)Fe(Et₂dtc)₃ measured in KBr disks resemble closely those of Fe(Et₂dtc)₃. There is possibly a small shift in the frequency of the C-N band (Fe(Et₂dtc)₃, 1483 ± 3 cm⁻¹; (R₄N)Fe(Et₂dtc)₃, 1478 ± 3 cm⁻¹), much smaller than the difference observed between Fe(Et₂dtc)₃ and (BF₄)Fe(Et₂dtc)₃.

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 Fe(R₂dtc)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°C), 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 coordination number of 6. Because of the increase in complexes with sulfur-binding ligands five-coordination is observed in bis(dithiocarbamate) complexes, whereas in iron(II) bis(dimethyldithiocarbamate) both five- and six-coordination can occur. The 10Dq value of R₄NFe(Et₂dtc)₃ found to be 8000 cm⁻¹, which is considerably lower than the value for iron(III) complexes, as expected.

Acknowledgment. We wish to thank Dr. J. S. of the preparation of the tris(dithiocarbamate) complexes and Mr. J. H. M. Gruyters for his cooperation in these experiments reported. The assistance of Miss R. F. W. of the experimental part of the work is gratefully acknowledged. This investigation was supported in part by the Foundation for Chemical Research (SON) with aid from the Netherlands Organization for the Promotion of Research (ZWO).

Registry No. Fe(Me₂dtc)₃, 41367-62-8; Fe(Et₂dtc)₃, 41367-64-0; Fe(n-Pr₂dtc)₂, 41429-87-4; Fe(n-Bu₂dtc)₂, 41444-80-8; Fe(n-Bu₄dtc)₂, 41371-75-9; Fe(Et₂dtc)₃, 41371-77-6; (Bu₄N)Fe(Et₂dtc)₃, 41371-78-2.

Figure 4. Electronic spectra of (a) (Ph₄P)Fe(Et₂dtc)₃, (b) Fe(Et₂dtc)₃, after oxidation in the absence of water, (c) (Et₄N)Fe(Et₂dtc)₃. All spectra were measured on KBr disks.