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Investigation of the Reactions of Iron(III) Halobisdithiocarbamates with Halogens: a Novel Series of Fluxional Homobinuclear Iron(III) Complexes with Two Different Coordination Spheres around the Magnetic Centers

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Abstract

In addition to the variety of products formed during the reaction of iron(III) halobisdithiocarbamates with halogens, some novel fluxional homobinuclear iron(III) complexes with two different coordination spheres around the magnetic centers have also been synthesized and studied. The formation of these products depends on the nature of both the molecular halogen and the reagent complex, as well as on the reaction conditions. The new compounds have been characterized chemically and by means of spectroscopic methods and magnetic susceptibility measurements. The volatility characteristics and thermogravimetric analysis data for the complexes were also studied. Finally, a general mechanism accounting for the variety of products formed in the reactions of iron(III) halobisdithiocarbamates with molecular halogens is proposed.

Introduction

The reactions of molecular halogens with dithiocarbamato metal complexes have attracted considerable interest in recent years [1–12] due to the variety of products formed. Depending on the nature of both the dithiocarbamato complex and the molecular halogen, the primary electron transfer reactions occurring are accompanied by a number of secondary processes which determine the nature of the final products. In general, these reactions can be classified into the following two types [13]: (i) the oxidation of the dithiocarbamato ligand by halogen into thiuramdisulfide (tds°) or dipositive trithiolane, and (ii) the oxidative addition reaction of halogen to the metal center of dithiocarbamato complexes. Despite these two types of electron transfer reactions, it has been demonstrated recently [14–17] that by reacting the iron(III) halobisdithiocarbamates, $[Fe(R_2dtc)_2X]$, with molecular halogens, X'_2, binuclear complexes formulated as $[Fe(R_2dtc)_2X]_2(\mu\text{-}X'_2)$ can be isolated. Mössbauer and magnetic measurements on this very interesting class of compounds, as well as an X-ray crystal structure determination [18] of the $2[Fe(Pyrrdtc)_2I]\cdot I_2$ complex, have established the presence of the molecular halogen in the form of a bridging unit mediating the formation of weakly coupled dimers with antiferromagnetic interaction. Moreover, extended Hückel calculations (EHMO) on a representative mononuclear complex bearing the same FeS_4X chromophore [16] clarified the nature of the orbital interactions; the loose association of the two isolated units were described by means of the molecular halogen in the binuclear complexes. These orbital interactions account for the formation of a linear [19] tetratomic bridging unit, $\{X\cdots X'\text{—}X'\cdots X\}^{2-}$, between the two paramagnetic centers, so that the overall result would be a loose dimeric association of the type $(R_2NCS_2)_2FeX\cdots X'\text{—}X'\cdots XFe(S_2CNR_2)_2$. Nevertheless, the salient feature of the aforementioned reaction is the effect of both the nitrogen substituent R and the halide ligand X on the type of products obtained [14, 15]. Therefore, we wish to report here the results of the study of some other unusual binuclear products, giving further insight into the reaction of halobis(N,N-disubstituted-dithiocarbamato)iron(III) complexes with halogens. Within this framework a general mechanism accounting for all possible products formed is also discussed.

Experimental

Physical Measurements

IR spectra were recorded in the 4000–250 cm^{-1} region on a Perkin-Elmer 467 spectrophotometer using KBr pellets or Nujol mulls. Electronic spectra were obtained on a Cary 17DX spectrophotometer using freshly prepared methylene chloride solutions. Mössbauer spectra were obtained with a conventional constant accelerator spectrometer. The source was 25-mCi of ^{57}Co in a copper matrix. Mass spectra were

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measured on a RMU-6L Hitachi Perkin-Elmer mass spectrometer with ionisation source of T-2p type operating at 70 eV. The thermogravimetric curves were obtained on a TGS-2 Perkin-Elmer thermobalance using nitrogen furnace atmosphere. Magnetic susceptibility measurements in solid state were done by the Faraday technique at different magnetic field strengths using $Hg[Co(SCN)_4]$ as the calibrant. Diamagnetic corrections were made using Pascal's constants. Conductivity measurements were done in a Wheatstone bridge Model RC $216B_2$ using 10^{-3} M solutions in acetone. Molecular weights were determined using a Perkin-Elmer molecular weight apparatus Model 115 in methylene chloride solutions. The elemental analysis of carbon, nitrogen and hydrogen was performed on a Perkin-Elmer 240B Elemental Analyser.

Starting Materials

All solvents were of reagent grade and were used without further purification in synthetic work. Tris(N,N-disubstituted-dithiocarbamato)iron(III) complexes were prepared and recrystallised as previously reported [20]. The halobis(N,N-dialkyldithiocarbamato)iron(III) complexes were obtained from the reaction between an iron(III) trisdithiocarbamate and aqueous hydrohalic acid [21, 22]. All the other reagents were obtained commercially.

Reactions of $[Fe(R_2dtc)_2X]$ with X'_2

The reactions of iron(III) halobisdithiocarbamates with molecular halogens were carried out as follows:

A solution of 2 mmol of the appropriate $[Fe(R_2dtc)_2X]$ complex in 50 ml of methylene chloride was treated with 1 mmol of Br_2 or I_2 dissolved in the same solvent and the reaction mixture was left for 5 h at room temperature under continuous magnetic stirring. After the addition of 50 ml of cyclohexane the solution was condensed to a small volume under reduced pressure, causing black crystals to separate. The resulting solid material was filtered off, washed with cyclohexane, recrystallised several times from methylene chloride–cyclohexane mixtures, and dried under vacuum.

Results and Discussion

Reaction of a solution of $[Fe(S_2CNR_2)_2X]$, where R_2 = Pyrr, R = Me, Et, Pr^i; X = Cl, Br (Pyrr = pyrrolidyl, Me = methyl, Et = ethyl, Pr^i = isopropyl), in methylene chloride with molecular halogens (2:1 molar ratios) rapidly gave clear solutions from which solid compounds of stoichiometry $Fe(S_2CNR_2)_2XX'$ (X' = Br, I) were isolated, either by precipitation with cyclohexane or by removal of solvent under reduced pressure. The dihalide complexes crystallise as black crystals, soluble in acetone, methylene chloride, acetonitrile and nitromethane, giving brownish solutions, and insoluble in benzene, cyclohexane, ether and water. The compounds are stable in absence of moist air, while in presence of atmospheric moisture they slowly hydrolyse. Data from elemental analyses, decomposition temperatures and molecular weights of the new compounds are given in Table I.

Taking into consideration that the aforementioned reaction consumes one mole of $[Fe(R_2dtc)_2X]$ reagent complex using only one-half mole of X'_2, both mononuclear or polynuclear compounds which agree exactly with the empirical formula $Fe(S_2CNR_2)_2XX'$ could be formed. Thus, one possibility is the formation of an iron(II) complex (1),

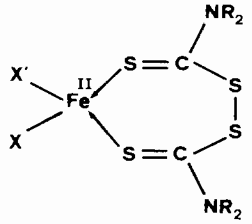

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TABLE I. Analytical Data for the New Complexes

Compound	Yield (%)	Melting Point[a] (°C)	Elemental Analyses			Molecular Weight
			%C	%N	%H	
$Fe_2(Me_2dtc)_2(tds^\circ)Cl_2Br_2$	75	210–212(d)[a]	17.62 (17.51)[b]	6.95 (6.81)	2.88 (2.94)	840 (823.3)
$Fe_2(Me_2dtc)_2(tds^\circ)Br_4$	70	184–186(d)	15.77 (15.80)	6.29 (6.14)	2.63 (2.65)	930 (912.2)
$Fe_2(Et_2dtc)_2(tds^\circ)Cl_2Br_2$	77	193–195(d)	25.61 (25.68)	5.80 (5.90)	4.34 (4.31)	960 (935.5)
$Fe_2(Et_2dtc)_2(tds^\circ)Br_4$	68	190–192(d)	23.52 (23.45)	5.45 (5.47)	3.83 (3.94)	1050 (1024.4)
$Fe_2(Pr^i_2dtc)_2(tds^\circ)Br_4$	74	168–170(d)	29.50 (29.58)	4.89 (4.93)	4.96 (4.97)	1070 (1036.6)
$Fe_2(Pyrrdtc)_2(tds^\circ)Cl_2Br_2$	77	160 162(d)	25.86 (25.90)	6.03 (6.04)	3.43 (3.48)	950 (927.4)
$Fe_2(Pyrrdtc)_2(tds^\circ)Cl_2I_2$	72	188–190(d)	23.48 (23.52)	5.47 (5.49)	3.12 (3.16)	1040 (1021.4)
$Fe_2(Pyrrdtc)_2(tds^\circ)Br_4$	65	166–168(d)	23.59 (23.63)	5.49 (5.51)	3.15 (3.17)	1030 (1016.3)
$Fe_2(Pyrrdtc)_2(tds^\circ)Br_2I_2$	76	172–174(d)	21.61 (21.63)	5.04 (5.05)	2.89 (2.91)	1140 (1110.3)

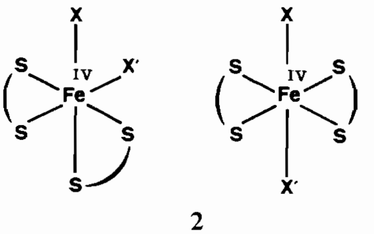
[a] d = decomposition. [b] Figures in parentheses are the calculated values.

TABLE II. Magnetic Data[a] and Mössbauer Parameters at 77 K for the Complexes

Compound	$\chi_M \times 10^6$ (cgsu)	μ_{eff}^{cor}(BM)	Outer doublet		Inner doublet	
			δ^b (mm s^{-1})	Δ(mm s^{-1})	δ^b (mm s^{-1})	Δ(mm s^{-1})
$Fe_2(Me_2dtc)_2(tds^\circ)Cl_2Br_2$	8677	4.64	0.69	2.84	0.73	0.68
$Fe_2(Me_2dtc)_2(tds^\circ)Br_4$	9609	4.82	0.70	2.73	0.69	0.74
$Fe_2(Et_2dtc)_2(tds^\circ)Cl_2Br_2$	8986	4.69	0.69	2.74	0.70	0.72
$Fe_2(Et_2dtc)_2(tds^\circ)Br_4$	10090	4.83	0.70	2.71	0.72	0.69
$Fe_2(Pr^i_2dtc)_2(tds^\circ)Br_4$	9388	4.80	0.68	2.83	0.69	0.74
$Fe_2(Pyrrdtc)_2(tds^\circ)Cl_2Br_2$	10369	5.00	0.69	2.74	0.70	0.69
$Fe_2(Pyrrdtc)_2(tds^\circ)Cl_2I_2$	9896	4.90	0.69	2.68	0.73	0.74
$Fe_2(Pyrrdtc)_2(tds^\circ)Br_4$	10102	4.96	0.70	2.73	0.72	0.74
$Fe_2(Pyrrdtc)_2(tds^\circ)Br_2I_2$	8056	4.75	0.69	2.81	0.68	0.74

[a] Temperature ≅ 22 °C. [b] Isomer shift relative to sodium nitroprusside.

with one-half of the oxidizing equivalents coming from the X'_2 and one-half from the metal reduction. It should be noted that the thiuramdisulfide might also bridge two Fe(II) centers to make a dimer or a polymer. Another possibility is the formation of a mononuclear iron(IV) complex (2) with *cis*- or *trans*-configuration,



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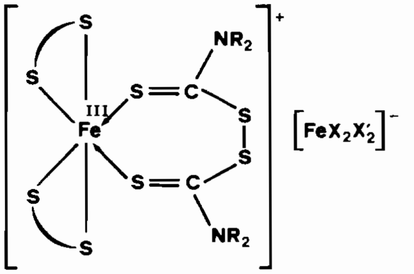
At first sight one would expect these iron(IV) complexes to be unstable, since the electron deficient Fe(IV) would be very unusual in an environment of electron rich R_2dtc^- ligands. Actually, both the magnetic susceptibilities and Mössbauer spectral data shown in Table II are not consistent with either an iron(IV) or an iron(II) complex; therefore these two possibilities can definitely be excluded. However, as will be discussed later on, these complexes might be formed as intermediates in the reactions studied.

The room-temperature magnetic moments for all the derivatives range from 4.64 to 5.00 BM, strongly suggesting the formation of iron(III) complexes in spin-mixed states (apparently between $S = 3/2$ and $S = 5/2$). Such a magnetic behaviour can be met either by mononuclear octahedral iron(III) complexes in an intermediate ligand field or by iron(III) complexes containing two iron(III) magnetic centers with different coordination spheres. However, osmometric molecular-weight measurements in methylene chloride (Table I) indicated the dimeric nature of the complexes; therefore the formation of mononuclear octahedral iron(III) complexes must be excluded. In keeping with the ligand oxidation idea, one possible structure which contains two iron(III) magnetic centers with different geometries is the following one (3):



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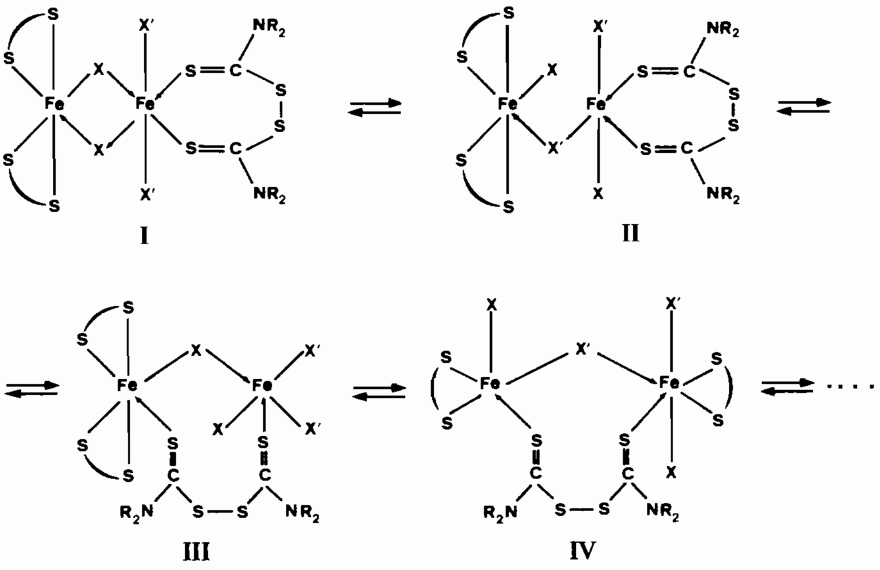
This involves oxidation of only half of the R_2dtc^- ligands; thus the iron remains as Fe(III). If this ligand oxidation takes place only on half of the $[Fe(R_2dtc)_2X]$ molecules, $[Fe(tds^\circ)XX'_2]$ complexes can be formed which, interacting with the unaffected halobisdithiocarbamates, may lead to the formation of neutral dimeric compounds containing bridging halide or thiuramdisulfide ligands. These complexes must be highly fluxional and could be represented by a number of structures some of which are shown in Scheme 1.

The dimeric structure seems to be the most likely one for the complexes under investigation, as the low values of the molar conductivity in anhydrous acetone (2–10 ohm^{-1} cm^2 mol^{-1}) indicate the non-electrolytic character of the compounds, thus excluding structure (3). Moreover, the dependence of the magnetic data on the magnetic field strengths calls for weak magnetic exchange interactions between the two iron centers, probably propagated through the bridging units, further supporting the dimeric nature of the complexes. This, however, is not particularly surprising since many studies, both experimental and theoretical, indicate that spin information is transmitted via the bridging ligands,



Scheme 1.

the mechanism being referred to as superexchange. Finally, the low magnetic moments observed both at low and high field strengths, as well as the slight decrease of the moments as the magnetic field decreases, are indicative of the operation of antiferromagnetism in these compounds.

Mössbauer spectra were recorded at liquid nitrogen temperature. The related data (δ, isomer shift; Δ, quadrupole splitting) for the new complexes are listed in Table II, and a representative spectrum is shown in Fig. 1. As might be expected from the observed magnetic moments, the spectra consisted of two doublets which demonstrate the presence of two inequivalent iron sites in the studied compounds – the one labeled α, with quadrupole splitting in the 2.68–2.84 mm s^{-1} range, indicating five-coordination [23], and the other, labeled β, with splitting in the range 0.68–0.74 mm s^{-1}, resembling closely the values normally observed for six-coordinated iron(III) chelates [24]. The experimental error in the quadrupole splittings was estimated to be ±0.03 mm s^{-1} on the basis of replicate measurements. The isomer shifts occur in the range 0.68–0.73 mm s^{-1} relative to sodium nitroprusside. These values are comparable to the shifts expected for iron(III) dithiocarbamates [23, 24]. The above observations are in accordance with the proposed structures of the complexes in the intramolecular ligand exchange pathway (Scheme 1) describing their fluxionality. The large difference in quadrupole splittings between α and β is understood in terms of a more symmetrical charge distribution (from both valence electrons and neighboring atoms) around the Fe^{3+} nucleus in β compared to α. This can conceivably result from the binding of one halide ligand of species α to the sixth available coordination site of Fe^{3+} in species β.

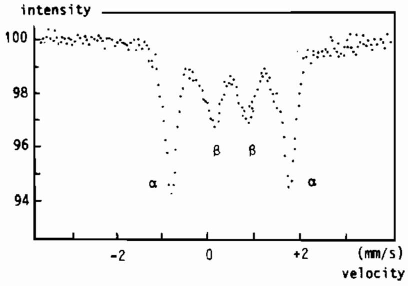


Fig. 1. Mössbauer spectrum of $Fe_2(Pyrrdtc)_2(tds^{\circ})Cl_2I_2$ measured at 77 K.

The spectroscopic and thermogravimetric analysis data of the complexes are also consistent with the proposed structures. The frequencies (cm^{-1}) of the most relevant absorption bands in the IR spectra of the studied compounds and their tentative assignments are presented in Table III. The $\nu(C\overset{\cdots}{-}N)$ and $\nu(C\overset{\cdots}{-}S)$ stretching frequencies fall in the range 1560–1525 cm^{-1} and 1020–970 cm^{-1}, respectively. The bidentate bonding mode of the dithiocarbamato ligands was established by the position of the $\nu(C\overset{\cdots}{-}N)$ band [25]. This band is shifted to higher frequencies compared to the corresponding halobisdithiocarbamate complexes [14, 26]. However, we observed peaks that could be ascribed to thiuramdisulfides [27], such as the weak band in the 400–500 cm^{-1} region, corresponding to the S–S stretching mode. Furthermore, single peaks have been observed in the range 370–350 cm^{-1}, which are likely to be due to metal–sulphur modes, according to the observed values for the dithiocarbamates of the first-row transition metals. Finally, the bands occurring in

TABLE III. The most Relevant IR Frequencies (cm^{-1}) of the Compounds Investigated and their Assignments (KBr discs)

Compound	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	ν(Fe–S)	ν(Fe–X)
$\mathrm{Fe_2(Me_2dtc)_2(tds^{\circ})Cl_2Br_2}$	1558vs, br^a	970s	355vs	305m
$\mathrm{Fe_2(Me_2dtc)_2(tds^{\circ})Br_4}$	1560vs, br	975s	368vs	290m
$\mathrm{Fe_2(Et_2dtc)_2(tds^{\circ})Cl_2Br_2}$	1530vs, br	995m	360vs	306w
$\mathrm{Fe_2(Et_2dtc)_2(tds^{\circ})Br_4}$	1538vs, br	998m	355vs	293m
$\mathrm{Fe_2(Pr^i_2dtc)_2(tds^{\circ})Br_4}$	1530vs, br	1015s	362vs	295m
$\mathrm{Fe_2(Pyrrdtc)_2(tds^{\circ})Cl_2Br_2}$	1530vs, br	1020s	350s	305w
$\mathrm{Fe_2(Pyrrdtc)_2(tds^{\circ})Cl_2I_2}$	1530vs, br	1000m	349s	310m
$\mathrm{Fe_2(Pyrrdtc)_2(tds^{\circ})Br_4}$	1525vs, br	998m	358vs	298m
$\mathrm{Fe_2(Pyrrdtc)_2(tds^{\circ})Br_2I_2}$	1529vs, br	1010s	351s	300w

^{a}vs = very strong, s = strong, m = medium, w = weak, br = broad.

the range 310–290 cm^{-1} were attributed to the iron–halogen stretching vibrations [28, 29], although they are at somewhat lower frequencies than in the five-coordinate derivatives. This is an indication for the coordination of more than one halogen to the metal atom, because the vibrational modes ν(Fe–X) are strongly dependent on the stereochemistry of the complex; an increase in the coordination number results in a decrease in the M–X stretching vibrations [26, 30]. The latter is further supported by the study of the reactions of these compounds with olefins. One would expect these complexes to be inactive towards their reaction with olefins; this was in fact the case, in contrast to the $\mathrm{[Fe(R_2dtc)_2X]_2(\mu\text{-}X'_2)}$ complexes of analogous stoichiometry which have been proven [16, 19] to be potential carriers of activated molecular halogens and therefore very reactive in halogen transfer reactions.

The thermogravimetric study of both the halobisdithiocarbamates and the compounds under investigation further confirms the formation of a dimeric association through the bridging ligands. For example, the thermograms of the $\mathrm{[Fe(Me_2dtc)_2Cl]}$ complex show three endothermic decompositions corresponding to a three-stage weight loss of 73.5%. A long plateau then results, from which there is evidence of FeS formation. The three weight losses occur at 270, 320 and 430 °C and can be attributed to loss of $\{\mathrm{2Me_2NCS}\}$ (Found: 53%; Calc.: 53.1%), {Cl} (Found: 11.0%; Calc.: 10.7%) and {S} (Found: 9.5%; Calc.: 9.6%), respectively. On the other hand, the thermograms of $\mathrm{Fe_2(Me_2dtc)_2(tds^{\circ})Cl_2Br_2}$ are composed of three weight losses, all of them endothermic at 230, 270 and 340 °C, which can be attributed to loss of $\{\mathrm{4Me_2NCS}\}$ (Found: 42.5%; Calc.: 42.8%), {2Br} (Found: 19.0%; Calc.: 19.4%) and {2Cl + 2S} (Found: 16.5%; Calc.: 16.4%), respectively.

In addition, the mass spectra of the compounds reveal the presence of a thiuramdisulfide ligand. The molecular ions of the dimeric species are not detected in the mass spectra. The absence of molecular ions can be attributed either to pyrolytic decomposition in the direct inlet under the high temperature which was used (200–280 °C), or to electron impact. However, in most of the spectra the ion $\mathrm{[Fe(R_2dtc)XX']^+}$ is present and can be regarded as direct fragment of the molecular ion upon elimination of a thiuramdisulfide ligand. This is further supported by the detection of a peak with a variable relative intensity (35–80%) due to $\mathrm{S_2^{+\bullet}}$ ion.

The electronic spectra of the studied compounds are complicated, exhibiting a number of overlapping intense bands in the ultra-violet and visible region. The complicated nature of the spectra prevents any simple classification and rationalization in terms of the ligand-field model. This is a general problem encountered in any ligand-field interpretation of the electronic spectra of many iron(III) halobisdithiocarbamate complexes [23, 26, 31]. However, in a previous paper [16] we have attempted to interpret the electronic spectrum of the $\mathrm{[Fe(Pr^i_2dtc)_2Br]}$ complex by means of EHMO quantum-chemical calculations. Assignments were made by associating the observed bands with the transitions they most nearly matched in energy. On the basis of these results it is evident that the spectra of the complexes under investigation are similar to those of the corresponding halobisdithiocarbamates. Therefore, it is reasonable to invoke the same assignments of the bands for the dihalide complexes as well. Their electronic spectral data and the assignments of the absorption bands are listed in Table IV.

Finally, the compounds were found to react further with excess bromine or iodine in methylene chloride solutions to give a greenish-yellow product of composition $\mathrm{Fe(S_2CNR_2)XX'_3}$. The results of spectroscopic and magnetic measurements suggest the presence of a positive dication with an s-tetrathian ring [5] and the iron(III) halogen anion, $\mathrm{FeXX'^-_3}$. This oxidation of the dithiocarbamato anion to a positive ion no longer coordinated to the metal has already been established for a number of dithiocarbamato metal complexes [4, 5].

TABLE IV. Electronic Spectral Data of the New Compounds in Methylene Chloride Solutions

Compound	Band I $L(\pi^*) \leftarrow L(\pi)$	Band II $M(d) \leftarrow L(\pi)$	Band III $L(\pi^*) \leftarrow L(\pi)$	Band IV $M(d) \leftarrow L(\pi)$	Band V $L(\pi^*) \leftarrow n(S)$	Band VI $M(d) \leftarrow L(\pi)$	Band VII $L(\pi^*) \leftarrow M(d)$	Band VIII $L(\pi^*) \leftarrow M(d)$
$\mathrm{Fe_2(Me_2dtc)_2(tds^{\circ})Cl_2Br_2}$	40.3[a] (4.85)[b]	37.4sh[c] (4.77)	35.8sh (4.65)	32.6 (4.52)	30.1 (4.37)	27.4 (4.09)	22.7 (4.10)	16.3 (3.83)
$\mathrm{Fe_2(Me_2dtc)_2(tds^{\circ})Br_4}$	39.1 (4.68)	37.6sh (4.48)	35.1sh (4.39)	32.5 (4.28)	29.4 (4.15)	25.7 (3.97)	22.0 (3.96)	16.3 (3.71)
$\mathrm{Fe_2(Et_2dtc)_2(tds^{\circ})Cl_2Br_2}$	39.4 (4.95)	37.6sh (4.86)	35.4sh (4.62)	32.5 (4.55)	29.8 (4.40)	26.1 (4.18)	22.4 (4.21)	16.3 (3.91)
$\mathrm{Fe_2(Et_2dtc)_2(tds^{\circ})Br_4}$	39.2 (4.80)	37.2sh (4.74)	35.3sh (4.50)	32.6 (4.37)	29.0 (4.25)	25.9 (4.17)	22.3 (4.12)	16.4 (3.91)
$\mathrm{Fe_2(Pr^{i}_2dtc)_2(tds^{\circ})Br_4}$	39.2 (4.67)	37.7sh (4.65)	35.4sh (4.40)	32.1 (4.38)	29.0 (4.19)	25.8 (4.06)	22.3 (4.06)	16.3 (3.81)
$\mathrm{Fe_2(Pyrrdtc)_2(tds^{\circ})Cl_2Br_2}$	39.4 (4.93)	37.4sh (4.87)	35.7sh (4.80)	32.6 (4.63)	28.6 (4.39)	26.0 (4.21)	22.4 (4.22)	16.7 (3.79)
$\mathrm{Fe_2(Pyrrdtc)_2(tds^{\circ})Cl_2I_2}$	40.2 (4.89)	37.7sh (4.77)	35.6sh (4.60)	32.6 (4.61)	30.1 (4.50)	27.0 (4.21)	22.4 (4.16)	16.3 (3.87)
$\mathrm{Fe_2(Pyrrdtc)_2(tds^{\circ})Br_4}$	40.0 (4.82)	37.7sh (4.73)	35.7sh (4.70)	32.5 (4.63)	29.0 (4.15)	26.0 (4.05)	22.2 (4.02)	16.2 (3.67)
$\mathrm{Fe_2(Pyrrdtc)_2(tds^{\circ})Br_2I_2}$	39.7 (4.75)	37.6sh (4.68)	35.7sh (4.54)	32.8 (4.45)	29.0 (4.24)	26.1 (4.14)	22.1 (4.10)	16.5 (3.80)

[a] ν/kK. [b] $\log \epsilon_{\mathrm{mol}}$. [c] sh = shoulder.

Combining our results on the reactions of iron(III) halobisdithiocarbamates with molecular halogens with those previously reported [14, 16], we can suggest the following general mechanism (Scheme 2) which accounts for the variety of products formed and studied to date. Thus, following pathway A, the formation [14, 15, 32] of the $[\mathrm{Fe(R_2dtc)_2XX'_2}]$ and $[\mathrm{Fe(R_2dtc)_2X'}]$ can be explained through a four-centered transition state. On the other hand, following pathway B, an unstable intermediate iron(IV) complex can be formed which is converted by intramolecular electron transfer to an iron(II) complex containing thiuramdisulfide as ligand. The latter can further react with excess halogen to afford the well-known positive dication [5] with an s-tetrathian ring and the iron(III) halogen anion. The same compound can be also formed through pathway C which involves as a first step the formation of the dihalide-bridged dimers [14–16]. Depending on the redox capacity of both the halogens and the dithiocarbamato ligands, an intramolecular electron transfer could take place resulting in the oxidation of half of the dithiocarbamate groups into thiuramdisulfide. In this case the fluxional dimeric compounds studied in the present paper are formed.

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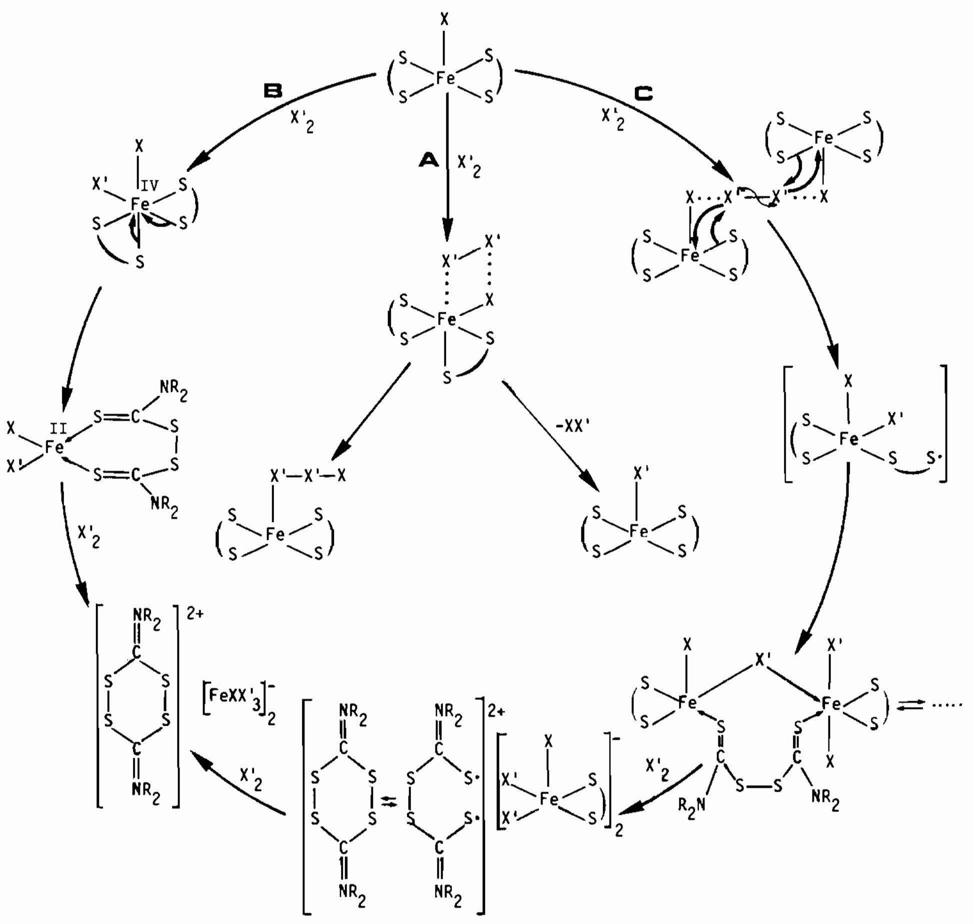

Scheme 2.

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