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THERMAL DECOMPOSITION OF SOME HOMOBINUCLEAR DIHALIDE-BRIDGED IRON(III) COMPLEXES

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Thermal studies by TG and DTG on some homobinuclear dihalide-bridged iron(III) complexes of the general type $[\mathrm{Fe(S_2CNR_2)_2}X]_2(\mu-X'_2)$ were carried out in air and nitrogen atmospheres. The apparent activation energies were determined by graphical methods and the TTN temperatures were calculated from the TG profiles. Finally, a possible mechanism of the decomposition is suggested on the basis of the pyrolysis and mass spectral data.

In previous papers, results have been reported on the reactions of molecular halogens (X'_2) with the square-pyramidal complexes $[\mathrm{Fe(S_2CNR_2)_2}X]$ (X = Cl, Br, I) [1–3]. The salient feature of these reactions is the effect of the alkyl substituent in the dithiocarbamato ligand on the composition of the products obtained [4, 5]. In this respect, a general mechanism accounting for the variety of products formed has been proposed [3].

In this paper, we focus our attention on the binuclear iron(III) complexes formulated [2] as $[\mathrm{Fe(S_2CNR_2)_2X}]_2(\mu-\mathrm{X}'_2)$, where R = Me, Et, Pr^i; X' = Br, I. Mössbauer and magnetic measurements on this very interesting class of compounds, as well as an X-ray crystal structure determination [6] of another derivative of this series containing the pyrrolidinyldithiocarbamato ligand, 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. In particular, the molecular halogen interacts weakly in an end-on fashion with the halide ligand of the mononuclear complexes, forming an extended tetratomic bridging unit, $\{X-X'-X'-X\}^{2-}$, between the two paramagnetic centres. Consequently, the binuclear complexes have been proved [7] to be potential carriers of activated molecular halogens and therefore very reactive in halogen-transfer reactions.

As an extension of our previous work [8–10] on thermal studies of metal diothiocarbamate complexes, a thermal investigation of the dihalide-bridged

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dithiocarbamates was undertaken. To date, such a study has not been performed for any iron(III) binuclear complexes, and it is of interest to compare their thermal behaviour to that of the corresponding halobisdithiocarbamates. Simultaneous TG/DTG studies in dynamic atmospheres of air and nitrogen are reported in this paper. The results of pyrolysis, E^* values for the main stage of decomposition derived from the Piloyan method [11], TTN calculations [12], mass spectral data, and a proposed mechanism of the decomposition reaction are also reported and discussed.

Experimental

The halobis(N,N-dialkyldithiocarbamato)iron(III) complexes were obtained from the reaction between an iron(III) trisdithiocarbamate and aqueous hydrohalic acid [13, 14]. The dihalide-bridged iron(III) complexes were prepared as previously reported [1, 2]; they were recrystallized several times from methylene chloride-cyclohexane mixtures, and dried under vacuum. The thermal decomposition was carried out on a TGS–2 Perkin–Elmer thermobalance at a heating rate of 5 deg/min, in the temperature range 20–1000°, with a sample mass of 5 mg and α-Al_2O_3 as reference. The measurements were performed in dynamic atmospheres of air and nitrogen.

X-ray powder diffraction analyses of the final residues were made with a Phillips PW 1130/00 X-ray diffractometer, using CuK_α radiation. For the determination of TTN, the areas of the TG curves were measured with a Coradi Cora-Senior planimeter.

The elemental analysis of carbon, nitrogen and hydrogen was performed on a Perkin–Elmer 240B microanalyzer. Infrared spectra were recorded in the 4000–250 cm^{-1} region on a Perkin–Elmer 467 spectrophotometer, using KBr pellets or Nujol mulls. Mass spectra were measured on an RMU–6 Hitachi Perkin–Elmer mass spectrometer with an ionization source of T–2p type operating at 70 eV. Molecular weights were determined in methylene chloride solutions, using a Perkin–Elmer 115 molecular weight apparatus.

Pyrolysis

The pyrolysis was carried out in dynamic nitrogen atmosphere, using the same technique as applied in our earlier work [8]. Highly volatile products of decomposition were collected in a liquid-air trap. The less volatile components of decomposition were separated by column chromatography, and were identified by spectroscopic methods, elemental analyses and molecular weight determinations.

Results and discussion

Thermal analysis

The thermoanalytical curves (TG and DTG) of some iron(III) halobisdithiocarbamates in dynamic nitrogen atmosphere are given in Figs 1–3. The temperature ranges and percentage mass losses of the decompositions, as well as the temperatures of the greatest rate of decomposition (DTG_{max}) and the theoretical percentage mass losses, are presented in Table 1. The obtained data of the complexes $[Fe(S_2CNR_2)_2X]$ show that the first decomposition stage occurs after the melting point and involves a sudden and considerable loss of mass (68–80%). This is attributed to the evolved moieties $\{2\ SCNR_2 + X\}$. However, the DTG curve of the iodo-derivative shows that the main decomposition process consists of two consecutive steps, the first involving the elimination of one thiocarbamoylo group

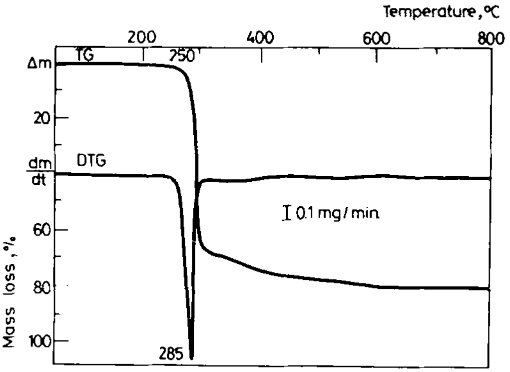


Fig. 1 Thermoanalytical curves for $[Fe(S_2CNEt_2)_2Cl]$ in nitrogen

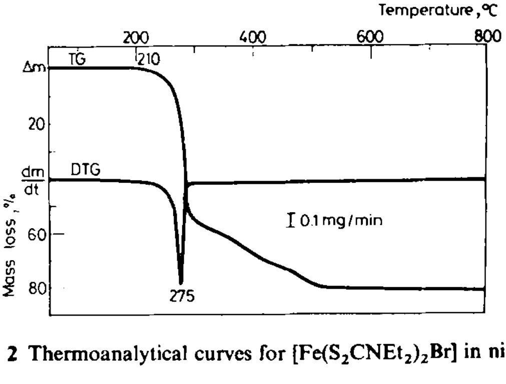


Fig. 2 Thermoanalytical curves for $[Fe(S_2CNEt_2)_2Br]$ in nitrogen

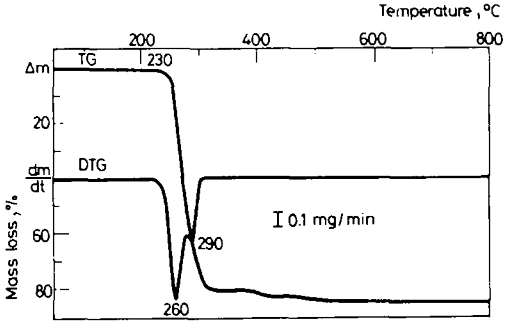


Fig. 3 Thermoanalytical curves for $[\mathrm{Fe(S_2CNPr^i_2)_2I}]$ in nitrogen

Table 1 Thermoanalytical results (TG/DTG) of some iron(III) halobisdithiocarbamates in nitrogen atmosphere

Complex	Stage	Temperature range, °C	$\mathrm{DTG_{max}}$, °C	Mass loss, %	Evolved moiety formula	Mass calcd., %
$[\mathrm{Fe(S_2CNEt_2)_2Cl}]$	1	250–310	285	68.5	$2\ \mathrm{SCNEt_2 + Cl}$	69.02
	2	310–410 + 410–590		9.0	S	8.25
	residue	>590		22.5	FeS	22.70
$[\mathrm{Fe(S_2CNEt_2)_2Br}]$	1	210–290	275	53.5	$\mathrm{S_2CNEt_2 + Br}$	52.78
	2	290–550		27.0	$\mathrm{SCNEt_2}$	26.85
	residue	>550		19.5	FeS	20.37
$[\mathrm{Fe(S_2CNPr^i_2)_2I}]$	1	230–310	290	79.5	$2\ \mathrm{SCNPr^i_2 + I}$	77.55
	α	230–280	260	50.0	$\mathrm{SCNPr^i_2 + I}$	50.64
	β	280–310	290	29.5	$\mathrm{SCNPr^i_2}$	26.91
	2	310–520		5.0	S	5.98
	residue	>520		15.5	FeS	16.44

plus a halogen atom, followed by the elimination of the thiocarbamoylo moiety of the remaining ligand. The possible intermediate after the first stage is considered to be $\mathrm{FeS_2}$, which is further converted into FeS upon elimination of one sulphur atom. The latter was found as final residue in nitrogen and was identified by X-ray powder diffraction analysis. Accordingly, the overall reaction path could be as follows:

$$[\mathrm{Fe(S_2CNR_2)_2X}] \xrightarrow{-\{\mathrm{SCNR_2}+X\}} \{\mathrm{SFe(S_2CNR_2)}\} \xrightarrow{-\{\mathrm{SCNR_2}\}} \mathrm{SFeS} \xrightarrow{-\{\mathrm{S}\}} \mathrm{FeS}$$

This process is analogous to the thermal decomposition of the halobis(piperidyldithiocarbamates) of As(III), Sb(III) and Bi(III) [10]. Moreover; the whole procedure of the thermal decomposition of the studied compounds appears to be strongly dependent on the nature of both the halogen and the substituents in the amine group. This fact was established by determining the TTN of the complexes from ,their TG curves in nitrogen atmosphere. TTN was proposed by Reich and Levi [12] as a criterion of the thermal stability of organic compounds. Thus, the TTN values (Table 4) for the halo derivatives indicated that the thermal stabilities of these complexes follow the sequence Cl > Br > I. This is in accordance with the strengths and the lengths of the Fe $-X$ bonds [15], as well as with the electronegativities of the halogens.

The thermal curves (TG and DTG) in air and nitrogen of the dihalide-bridged iron(III) complexes are depicted in Figs 4–11. The thermal analysis data obtained

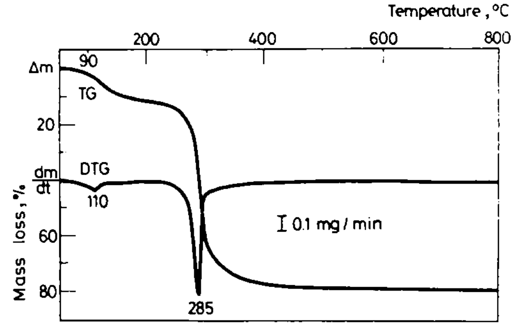


Fig. 4 Thermoanalytical curves for $[\mathrm{Fe(S_2CNMe_2)_2Cl}]_2(\mu\text{-}\mathrm{I_2})$ in nitrogen

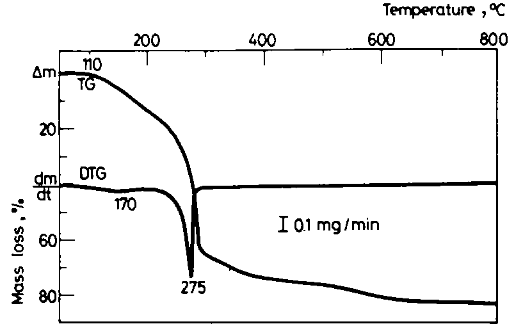


Fig. 5 Thermoanalytical curves for $[\mathrm{Fe(S_2CNEt_2)_2Cl}]_2(\mu\text{-}\mathrm{I_2})$ in nitrogen

Table 2 Thermoanalytical results (TG/DTG) of some dihalide-bridged iron(III) binuclear complexes in nitrogen atmosphere

Complex	Stage	Temperature range, °C	DTG_{max}, °C	Mass loss, %	Evolved moiety formula	Mass calcd., %
$[Fe(S_2CNMe_2)_2Cl]_2(\mu\text{-}I_2)$	1	90–160	110	10.0	$SCNMe_2$	9.59
	2	160–330	285	61.0	$2\ S_2CNMe_2 + I_2 + SCNMe_2$	63.44
	3	330–450		7.5	2 Cl	7.74
	residue	>460		21.5	2 FeS	19.19
$[Fe(S_2CNEt_2)_2Cl]_2(\mu\text{-}I_2)$	1	110–200	170	14.0	S_2CNEt_2	14.38
	2	200–290	275	51.0	$S_2CNEt_2 + I_2 + + SCNEt_2$	50.33
	3	290–500		11.5	$SCNEt_2$	11.27
	4	500–650		6.5	2 Cl	6.90
	residue	>650		17.0	2 FeS	17.10
$[Fe(S_2CNPr^i_2)_2Cl]_2(\mu\text{-}I_2)$	1	110–240	230	54.0	$2\ S_2CNPr^i_2 + I_2$	53.06
	α	110–165	150	6.5	CS_2	6.66
	β	165–240	230	47.5	$S_2CNPr^i_2 + I_2 + + NPr^i_2$	46.40
	2	240–390	290	25.0	$2\ SCNPr^i_2$	25.40
	3	390–690		6.0	2 Cl	6.22
	residue	>690		15.0	2 FeS	15.42
$[Fe(S_2CNPr^i_2)_2Br]_2(\mu\text{-}I_2)$	1	80–165	105, 150	14.5	$S_2CNPr^i_2$	14.30
	α	80–130	105	6.3	CS_2	6.17
	β	130–160	150	7.7	NPr^i_2	8.13
	2	165–270	230	58.5	$S_2CNPr^i_2 + I_2 + + 2\ SCNPr^i_2$	58.35
	3	270–610		12.5	2 Br	13.00
	residue	>610		14.5	2 FeS	14.30
$[Fe(S_2CNPr^i_2)_2Cl]_2(\mu\text{-}Br_2)$	1	80–280	230, 260	76.0	$2\ S_2CNPr^i_2 + Br_2 + + 2\ SCNPr^i_2$	75.98
	α	80–250	230	48.5	$2\ S_2CNPr^i_2 + Br_2$	48.88
	β	250–280	260	27.5	$2\ SCNPr^i_2$	27.10
	2	280–350		6.5	2 Cl	6.78
	residue	>350		16.5	2 FeS	16.80
$[Fe(S_2CNPr^i_2)_2I]_2(\mu\text{-}Br_2)$	1	100–170	160	14.5	$S_2CNPr^i_2$	14.30
	2	170–235	220	13.0	Br_2	13.00
	3α	235–290	250	46.0	$S_2CNPr^i_2 + 2\ I + + SCNPr^i_2$	46.55
	β	290–330		12.0	$SCNPr^i_2$	11.70
	residue	>330		14.5	2 FeS	14.30

Table 3 Thermoanalytical results (TG/DTG) of some dihalide-bridged iron(III) binuclear complexes in air atmosphere

Complex	Stage	Temperature range, °C	DTG$_{max}$, °C	Mass loss %	Evolved moiety formula	Mass calcd., %
$[Fe(S_2CNEt_2)_2Cl]_2(\mu\text{-}I_2)$	1	80–210	185	54.0	$2\ S_2CNEt_2 + I_2$	53.44
	2α	210–330	~300	11.5	$SCNEt_2$	11.27
	β	330–440		6.5	2 Cl	6.89
	3	440–670		5.0	gradual oxidation of FeS_n (n = 1, 2)	—
	residue	>670		23.0	FeO, $FeSO_4$	—
$[Fe(S_2CNPr^i_2)_2Cl]_2(\mu\text{-}I_2)$	1	100–200	175	27.5	$S_2CNPr^i_2 + {} + SCNPr^i_2$	28.04
	α	100–160	150	6.5	CS_2	6.66
	β	160–200	175	21.0	$SCNPr^i_2 + {} + NPr^i_2$	21.38
	2	200–255	215	21.5	I_2	22.26
	3	250–310	~290	10.0	$SCNPr^i_2$	12.62
	4	400–550 + 550–650	455	29.0	$(SCNPr^i_2 + 2\ Cl) + {}$ + gradual oxidation	18.84
	residue	>650		12.0	2 FeO	12.62

Table 4 Activation energy's values, E^*, and TTN temperatures of the investigated compounds

Complex	TTN, °C	Activation energy, E^*, kcal/mol	
		TG	DTG
$[Fe(S_2CNEt_2)_2Cl]$	240	68	66
$[Fe(S_2CNEt_2)_2Br]$	212	49	—
$[Fe(S_2CNPr^i_2)_2I]$	210	52	50
$[Fe(S_2CNMe_2)_2Cl]_2(\mu\text{-}I_2)$	93	34	39
$[Fe(S_2CNEt_2)_2Cl]_2(\mu\text{-}I_2)$	106	22	24
$[Fe(S_2CNPr^i_2)_2Cl]_2(\mu\text{-}I_2)$	108	18	35
$[Fe(S_2CNPr^i_2)_2Br]_2(\mu\text{-}I_2)$	85	23	33
$[Fe(S_2CNPr^i_2)_2Cl]_2(\mu\text{-}Br_2)$	82	27	—
$[Fe(S_2CNPr^i_2)_2I]_2(\mu\text{-}Br_2)$	90	40	40

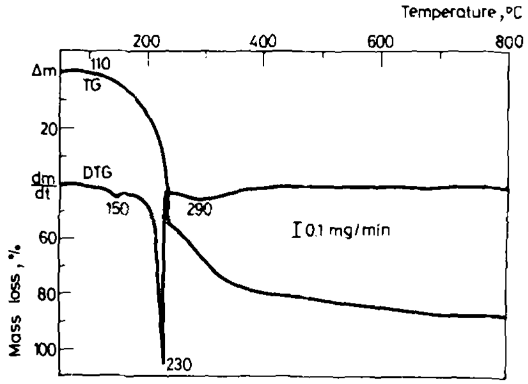


Fig. 6 Thermoanalytical curves for $[Fe(S_2CNPr^i_2)_2Cl]_2(\mu\text{-}I_2)$ in nitrogen

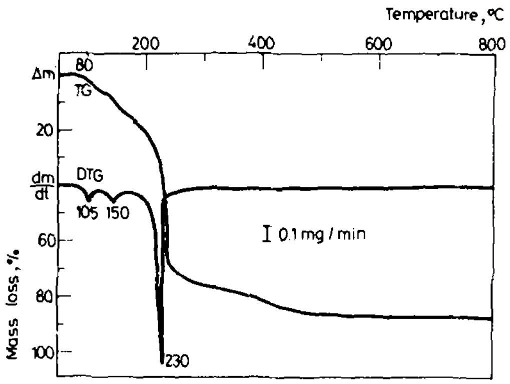


Fig. 7 Thermoanalytical curves for $[Fe(S_2CNPr^i_2)_2Br]_2(\mu\text{-}I_2)$ in nitrogen

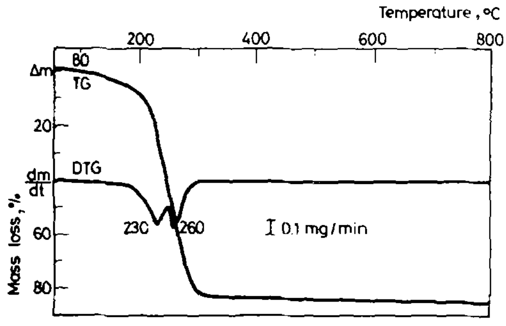


Fig. 8 Thermoanalytical curves for $[Fe(S_2CNPr^i_2)_2Cl]_2(\mu\text{-}Br_2)$ in nitrogen

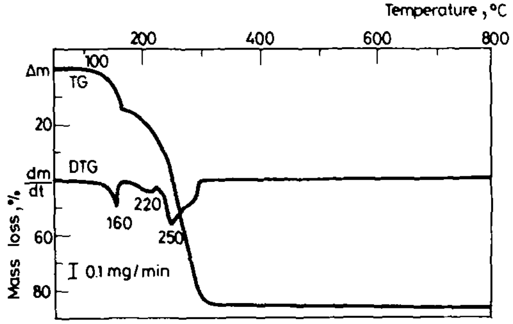


Fig. 9 Thermoanalytical curves for $[Fe(S_2CNPr^i_2)_2I]_2(\mu\text{-}Br_2)$ in nitrogen

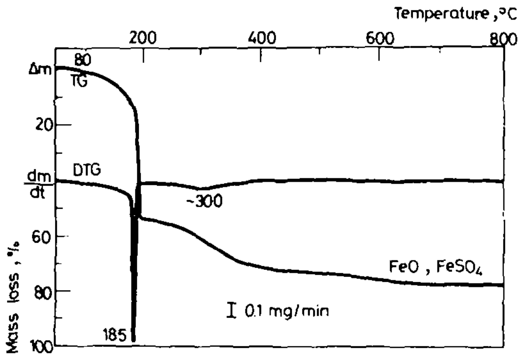


Fig. 10 Thermoanalytical curves for $[Fe(S_2CNEt_2)_2Cl]_2(\mu\text{-}I_2)$ in air

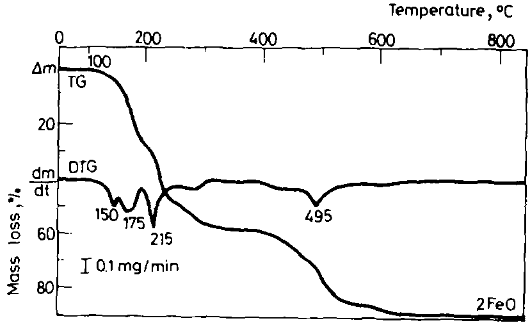


Fig. 11 Thermoanalytical curves for $[Fe(S_2CNPr^i_2)_2Cl]_2(\mu\text{-}I_2)$ in air

from these curves are given in Tables 2 and 3. From the TG profiles it is obvious that the main decomposition stage is similar in air and nitrogen. The considerable mass losses in this stage involve the elimination of two dithiocarbamato groups plus the molecular halogen bridging unit. However, in several cases the DTG curves show that the main decomposition process consists of two consecutive steps. It is logical to assume that carbon disulphide is primarily evolved after breaking of the metal-sulphur bond, which occurs first, followed by elimination of the amine group, plus one dithiocarbamato group and the molecular halogen moiety. The next stage of decomposition involves the elimination of one or two thiocarbamoylo moieties of the remaining ligands, followed by rupture of the Fe–X bond and elimination of the halide ligand. The intermediate after the second step is considered to be possibly XFeS (X = Cl, Br, I), which yields FeS as final residue. In air, the third step of decomposition involves the gradual oxidation of the metal sulphides [16]. According to the results of X-ray powder diffraction analysis and infrared spectroscopy, the final residue corresponds to mixed FeO and $FeSO_4$.

Conclusively, we can say that our results show the dependence of the whole procedure of thermal decomposition of the compounds under investigation on the nature of the molecular halogen bridging unit, and on the alkyl substituent in the dithiocarbamato ligand. This was established by determining the TTN values of the complexes from their TG curves in nitrogen atmosphere. Thus, the TTN values (Table 4) for the dihalide-bridged complexes indicated that the more stable ones are those containing a molecular iodine bridging unit, whereas their decomposition temperatures tend to decrease from isopropyl to methyl derivatives, in accordance with the decreasing basicity of the corresponding amines.

Apparent activation energy (E^*)

The activation energies of the studied compounds were calculated graphically from the TG and DTG curves by Piloyan's two methods [11, 17]. The E^* values are referred to the main decomposition stage in nitrogen and are given in Table 4. As expected, the E^* values of the dihalide-bridged complexes are fairly close, since the metal is the same in every case. Moreover, the calculated E^* values of the complex $[Fe(S_2CNPr^i_2)_2I]_2(\nu\text{-}Br_2)$, for the first and the second decomposition stage separately, indicated that the activation energy for the elimination of one dithiocarbamato group (16 kcal/mol from TG and 27 kcal/mol from DTG) is somewhat smaller than that derived from the elimination of the molecular halogen (31 kcal/mol from TG and 28 kcal/mol from DTG). This fact may lead to the conclusion that the interaction of the molecular halogen with the halide ligand of the mononuclear complexes causes the weakness of one metal-sulphur bond.

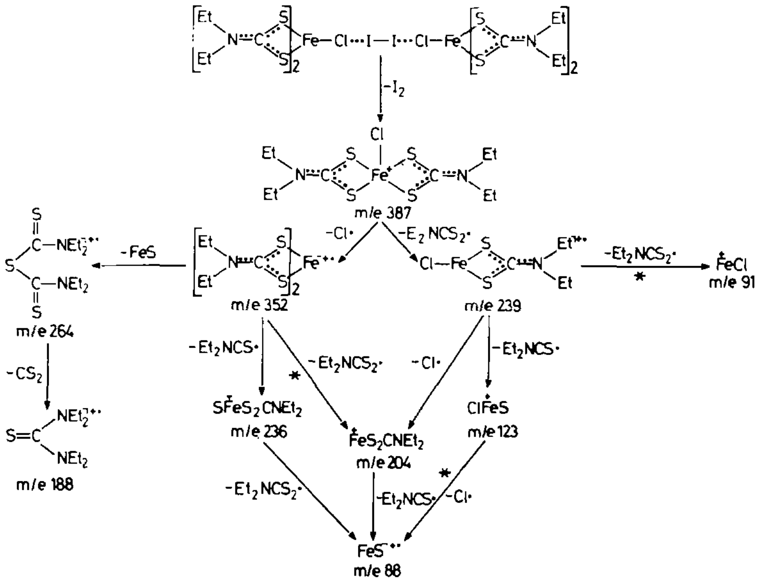
Mass spectra

Table 5 gives the most relevant mass spectral peaks of the dihalide-bridged dithiocarbamates under study. 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 used (200–280°), or to electron impact. However, in all spectra the ion $[Fe(S_2CNR_2)_2X]^+$ is present and can be regarded as the direct fragment of the molecular ion upon elimination of the molecular halogen bridging unit. This is supported by the detection of a peak with variable relative intensity (54–100%) due to the $X'_2{}^{\rceil +\cdot}$ ion. For the complexes $[Fe(S_2CNR_2)_2X]_2(\mu\text{-}I_2)$ the base peak of the spectra corresponds to the $I_2^{\rceil +\cdot}$ ion.

Table 5 Most relevant mass spectral peaks of some dihalide-bridged iron(III) binuclear complexes

Complex	*m/e* (R.I.)†
$[Fe(S_2CNMe_2)_2Cl]_2(\mu\text{-}I_2)$	28 (63), 32 (61), 35 (12),37 (4), 41 (32), 44 (16), 59 (10), 73 (17), 76 (84), 88 (25), 91 (3), 105 (2), 120 (3), 123 (2), 127 (53), 132 (3), 176 (4), 208 (7), 211 (< 1), 254 (100), 296 (16), 331 (1).
$[Fe(S_2CNEt_2)_2Cl]_2(\mu\text{-}I_2)$	27 (56), 28 (50), 29 (58), 30 (78), 32 (40), 35 (10), 37 (3), 43 (20), 44 (33), 56 (16), 58 (74), 59 (15), 60 (6), 72 (12), 76 (25), 88 (16), 91 (3), 116 (23), 123 (7), 127 (61), 148 (21), 188 (4), 204 (2), 236 (1), 239 (< 1), 254 (100), 264 (2), 352 (1), 387 (< 1).
$[Fe(S_2CNPr^i_2)_2Cl]_2(\mu\text{-}I_2)$	29 (16), 32 (24), 35 (16), 37 (8), 39 (70), 41 (64), 43 (89), 44 (99), 58 (22), 76 (32), 86 (69), 88 (14), 91 (3), 101 (23), 123 (6), 127 (96), 144 (25), 176 (13), 232 (3), 244 (2), 254 (100), 264 (2), 267 (1), 320 (2), 408 (< 1), 443 (< 1).
$[Fe(S_2CNPr^i_2)_2Br]_2(\mu\text{-}I_2)$	29 (21), 32 (24), 39 (83), 41 (98), 43 (95), 44 (97), 58 (32), 76 (38), 79 (8), 81 (5), 86 (61), 88 (14), 101 (66), 127 (99), 144 (26), 167 (4), 176 (13), 232 (3), 244 (2), 254 (100), 264 (3), 311 (2), 320 (2), 408 (1), 487 (< 1)
$[Fe(S_2CNPr^i_2)_2Cl]_2(\mu\text{-}Br_2)$	29 (22), 32 (29), 35 (12), 37 (5), 39 (100), 41 (97), 43 (99), 44 (62), 58 (27), 76 (37), 79 (8), 81 (4), 86 (58), 88 (12), 91 (5), 101 (96), 123 (5), 144 (19), 158 (39), 162 (57), 176 (14), 232 (5), 244 (2), 264 (3), 267 (2), 320 (2), 408 (< 1), 443 (4).
$[Fe(S_2CNPr^i_2)_2I]_2(\mu\text{-}Br_2)$	29 (19), 32 (28), 39 (100), 41 (92), 43 (90), 44 (26), 58 (36), 76 (32), 79 (11), 81 (15), 86 (72), 88 (14), 101 (95), 127 (12), 144 (22), 158 (44), 162 (54), 176 (12), 183 (2), 215 (1), 232 (3), 244 (2), 264 (3), 320 (2), 359 (1), 408 (2), 535 (< 1).

† R.I. = Relative Intensity



Scheme 1 Possible fragmentation pattern of the $[Fe(S_2CNEt_2)_2Cl]_2(\mu\text{-}I_2)$ complex

The highest mass number ions observed for all compounds, which might be direct fragments of the $[Fe(S_2CNR_2)_2X]^+$ ion, are those of general formulae $[Fe(S_2CNR_2)_2]^{+\cdot}$ and $[Fe(S_2CNR_2)X]^{+\cdot}$. The latter is probably due to the cleavage of one Fe—S bond and the loss of a dithiocarbamate radical. However, we might expect a low relative abundance of these ions, considering the known thermal instability of similar compounds [18, 19] and organometallic compounds in general. A number of daughter ions, besides the ones mentioned above, were also detected. The genesis of these ions is demonstrated by the general fragmentation pattern shown in Scheme 1. Most of the fragmentation processes were metastable supported. For example, in the case of the complex $[Fe(S_2CNEt_2)_2Cl]_2(\mu\text{-}I_2)$ the existence of metastable peaks at $m^* = 118.2$, $m^* = 62.9$, and $m^* = 34.6$ confirms the following fragmentations:

$$\mathrm{Fe(S_2CNEt_2)_2^{\urcorner\,+\cdot}} \xrightarrow[*]{-\mathrm{Et_2NCS_2}\cdot} \overset{+}{\mathrm{Fe}}\mathrm{S_2CNEt_2}$$

m/e 352 m/e 204

$$\mathrm{Cl}\overset{+}{\mathrm{Fe}}\mathrm{S} \xrightarrow[*]{-\mathrm{Cl}} \mathrm{FeS^{\urcorner\,+\cdot}}$$

m/e 123 m/e 88

$$\mathrm{Fe(S_2CNEt_2)Cl^{\urcorner\,+\cdot}} \xrightarrow[*]{-\mathrm{Et_2NCS_2}\cdot} \overset{+}{\mathrm{Fe}}\mathrm{Cl}$$

m/e 239 m/e 91

Moreover, the fragmentations of the dithiocarbamate moiety are similar in all the complexes. Thus, the ligand Et_2NCS_2, m/e 148, loses a sulphur atom, followed by stepwise dissociation of the methylene groups to give the $NCS^{\urcorner +\cdot}$ ion. Analogous processes have already been proposed [18–20] for several metal dithiocarbamate complexes.

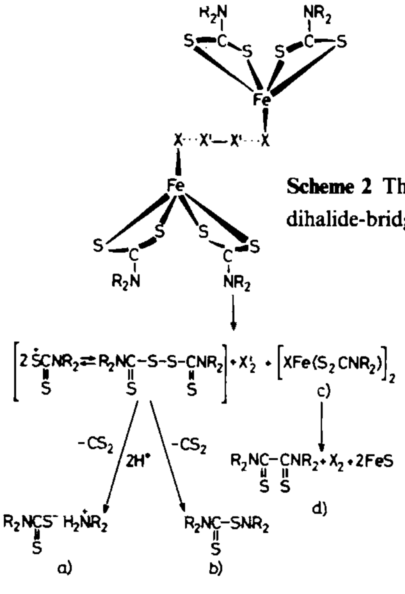
Considering the above results, it becomes evident that the fragmentation patterns derived from the mass spectral study of the investigated compounds are in good agreement with the thermal decomposition results.

Pyrolysis

A sample of the complex $[Fe(S_2CNEt_2)_2Cl]_2(\mu\text{-}I_2)$ was heated in nitrogen atmosphere up to the temperature at the end of the main decomposition stage (290°) The volatile products formed during the pyrolysis were carbon disulphide, iodine, and a yellow liquid which turned out to be tetraethyldithiocarbamyl sulphenamide [21]. The diethylammonium salt of diethyldithiocarbamic acid was also isolated as a white solid, which is unstable in air and decomposes to diethylamine [22]. After the completion of pyrolysis at 290°, a black residue was left at the bottom of the flask, in which chlorine anions were detected. After heating up to 450°, this residue affords a solid which contains mainly metal sulphide and elemental carbon (1–10%).

Mechanism

By combining the thermogravimetric analysis data and the pyrolysis results on the dihalide-bridged iron(III) complexes, we can propose a possible mechanism for their thermal decomposition. According to Scheme 2, this mechanism involves the



Scheme 2 Thermal decomposition of the dihalide-bridged iron(III) binuclear complexes

homolytic dissociation of two dithiocarbamato groups and their subsequent reaction to form thiuram disulphide. This is thermally unstable and decomposes further to yield carbon disulphide and either dithiocarbamate salt (a), $R_2NC(:S)\bar{S}H_2\overset{+}{N}R_2$, or suphenamide (b), $R_2NC(:S)SNEt_2$. The molecular halogen bridging unit is also evolved, whereas the possible intermediate (c), $[XFe(S_2CNR_2)]_2$, is unstable and consequently can not be isolated. This intermediate can decompose further to give molecular halogen, with FeS as final residue. Interestingly, no CS_2 was detected among the pyrolysis products of this intermediate. Thus, we presume that dithio-oxamide (d), $R_2NC(:S)C(:S)NR_2$, may be produced [23].

* * *

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Zusammenfassung — Einige homobinukleare Eisen(III)-Komplexe mit Dihalidbrücken der allgemeinen Formel $[Fe(S_2CNR_2)_2X]_2(\mu\text{-}X'_2)$ wurden mittels TG und DTG in Luft und Stickstoffatmosphäre untersucht. Die scheinbaren Aktivierungsenergien wurden nach graphischen Methoden aus den TG-Profilen bestimmt. Ein möglicher, auf pyrolytischen und massenspektrometrischen Daten basierender Zersetzungsmechanismus wird vorgeschlagen.

Резюме — Методом ТГ и ДТГ изучено термическое разложение в атмосфере воздуха и азота некоторых гомодвухядерных комплексов трехвалентного железа общей формулы $[Fe(S_2CNR_2)_2X]_2\ (\mu - X'_2)$ с мостиковой связью между галоидами. Кажущиеся энергии активации были определены графическим методом, а ТТН температуры были вычислены из профилей ТГ-кривых. На основе результатов пиролиза и масс-спектрометрических данных обсужден возможный механизм разложения.